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ANALYTICAL EDITION

Industrial AND ENGINEERING Chemistry

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HARRISON E. HOWE, EDITOR

Reduction of Antimonic Acid in Hydrochloric Acid Solution with Mercury

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McCAY and Anderson (*2*) have shown that ferric salts and vanadic acid are completely reduced, the former to the ferrous, the latter to the vanadyl condition, when their hydrochloric acid solutions are shaken for 5 minutes in the presence of mercury. They have also shown that chromic, molybdic, and antimonic acids in dilute hydrochloric acid solution are more or less reduced when subjected to a similar treatment.

Especially interesting is the behavior of solutions of antimonic acid in the presence of mercury. The author has made a long and detailed study of this reaction, and has succeeded in establishing the conditions under which the reduction of the element from the quinquivalent to the trivalent state can in all cases be made quantitative.

STUDY OF THE REACTION

When a solution of antimonic acid, prepared by oxidizing one of antimonious chloride or sulfate with potassium bromate, and containing one-fourth or one-third its volume of concentrated hydrochloric acid (sp. gr. 1.19) is shaken violently for 5 minutes in the presence of mercury, all the antimonic is reduced to antimonious acid:

$$Sb^{+++++} + 2Cl^- + 2Hg = Sb^{+++} + 2HgCl$$

Owing to the air present a small amount of mercuric chloride is also formed:

$$2HgCl + 2HCl + O = 2HgCl_2 + H_2O$$

If, however, the solution be one of dihydrogen potassium pyroantimoniate, the reduction of the antimony to the trivalent state is, in the circumstances, never complete. Even when such a solution is heated on the water bath for 15 to 20 minutes, and shaken violently off and on for one hour, quinquivalent antimony can be detected in the filtrate from the mercurous chloride and finely divided mercury. Better results may be obtained by placing the well-stoppered bottle containing the solution and the mercury in a powerful shaking machine and agitating it for one hour. While the reduction here is generally complete, sometimes it is not, for in some instances over a milligram of antimony may remain in the higher state of oxidation. Three very pure samples of the pyro-salt from three well-known houses were used in this work. Their solutions all behaved in an analogous manner. The qualitative test for minute amounts of quinquivalent in the presence of relatively large amounts of trivalent antimony, according to the method of Bunsen, as ordinarily carried out, is apt to prove misleading (*5*), for not only does boiled and cooled water acidified with hydrochloric acid assume in a few minutes a pronounced yellow tint when potassium iodide, free from iodate, is added to it, but when antimonious chloride is also present the addition of the potassium iodide occasions the immediate formation of antimonious iodide, or oxyiodide which gives the solution a faint yellow color. Since, however, acid water alone when saturated with carbon dioxide and kept under an atmosphere of this gas and in the dark remains colorless or barely yellow for hours after the addition of potassium iodide, satisfactory results were obtained by proceeding as follows: The filtrate from the mercury and mercurous chloride was caught in a little bottle holding about 100 cc. and provided with a stopper ground so as to furnish an airtight joint (*3*). A brisk current of pure carbon dioxide was introduced, permitted to traverse the liquid for ten minutes, a crystal of potassium iodide about the size of a pea was dropped in while the gas was still passing, the delivery tube was withdrawn, and the bottle was instantly stoppered. Since the amount of antimonious chloride in the filtrate was known within one or two milligrams, 100 cc. of a solution containing this amount of the pure chloride and the specified quantity of concentrated hydrochloric acid were subjected at the same time to the same treatment. After the bottles had stood for a few minutes in the dark and the colors of the two solutions were compared, that of the former appeared the darker if it contained quinquivalent antimony. In this way 0.1 mg. of Sb^V could be detected in the presence of relatively large amounts of Sb^{III}.

Practically no reaction occurs when water and pure mercury are shaken together; the water remains clear and the metal is barely tarnished. If hydrochloric acid be present the liquid remains perfectly clear for 5 minutes, and then becomes suddenly hazy owing to a separation of the highly characteristic silky needle form of mercurous chloride. The amount increases as the shaking is continued, and at the end of an hour it is comparatively large:

$$2Hg + O = Hg_2O \text{ and } Hg_2O + 2HCl = 2HgCl + H_2O$$

In an atmosphere of pure carbon dioxide no change occurs,

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even when the dilute hydrochloric acid and mercury are shaken together for hours.

The mercurous chloride equivalent to the antimonic acid reduced along with that formed by the interaction of the mercury and oxygen of the air may be the cause of the persistency with which solutions of the pyro-salt resist complete reduction. The globules into which the greater part of the mercury breaks, as well as the rest of the metal, get covered with a protecting skin of mercurous chloride. Of course during the shaking of the contents of the bottle some of these skins are occasionally knocked off, but they immediately reform. At all events the reductions in an atmosphere of carbon dioxide where no additional mercurous chloride can be formed are invariably complete at the end of an hour's shaking in the machine. Although this time may seem unnecessarily long it must be borne in mind that, in general, we have no means for knowing offhand the form in which the antimonic acid in a solution is present. We possess, indeed, no definite information in regard to the so-called ortho-, meta-, and pyro-antimonic acids, the methods for preparing them, the circumstances in which they may be converted into one another, and the tests for distinguishing between them. For this reason, in the quantitative work which follows, the author has always assumed that the solutions contained some or all of the acid in the form least easily reduced.

Arsenic and stannic acids in hydrochloric acid solutions undergo no change when shaken for hours in the presence of mercury.

Quantitative Results

The bottle used in this work is cylindrical in shape, 12 cm. high from the bottom to the shoulder, 6 cm. in diameter, and holds about 150 cc. It is provided with a glass stopper which fits air-tight, and it is charged with 20 to 25 cc. of pure mercury. So charged it will be referred to as the reductor. The materials used in preparing the test solutions were the best grades furnished by the Kahlbaum house.

Solution A. 2.2063 grams of powdered antimony were treated in a covered dish with 50 cc. of concentrated sulfuric acid which was heated to gentle boiling. When solution was complete the flame of the burner was lowered and the acid allowed to fume strongly for about 15 minutes, so as to get rid of all traces of sulfur dioxide. Water was added, and the turbid liquid was cooled, transferred to a 500-cc. flask, and diluted with concentrated hydrochloric acid and water to the mark. So prepared the solution contained one-fourth its volume of concentrated hydrochloric acid. The antimony was determined in 25 cc. by the Györy method. Antimony found equaled 0.1103 gram, whereas the theory calls for 0.1103 gram.

Solution B. 8.6444 grams of dihydrogen potassium pyro-antimoniate were dissolved in a liter flask on the water bath in 200 cc. of concentrated hydrochloric acid, water was added, the solution cooled and diluted to the mark with water and concentrated hydrochloric acid. The solution contained about one-third its volume of this acid. The large amount of acid is necessary to keep the solution clear indefinitely. The antimony in 25 cc. was determined by heating the strongly acidified solution with a large excess of sulfurous acid in a pressure bottle for one hour in the boiling water bath, evaporating the liquid to somewhat less than one-half its volume, cooling it, diluting to 200 cc., and titrating the antimony with 0.1 *N* potassium bromate. (The method is similar to that used for reducing arsenic acid solutions, *1*.) A blank was made in the same way, using the same amount of sulfurous and hydrochloric acids. After correcting for the amount of bromate used in the blank (from 0.15 to 0.2 cc.), the antimony was calculated, and found to be (1) 0.1067 and (2) 0.1068 gram. As a check the antimony was also determined according to an indirect method highly recommended by Rose (*4*), and found to be 0.1067 gram. The element was calculated from the weight of potassium chloride obtained.

The 0.1 *N* potassium bromate used in the Györy method was standardized against the Bureau of Standards arsenious oxide, which was also used in determining arsenic and antimony in the presence of each other.

The author has had over three years of experience with the Györy method, and has no hesitancy in pronouncing it the best of all methods for determining antimony. If plenty of hydrochloric acid be present, the same results are obtained when the volume of the solution to be titrated is 50, 100, or 200 cc. In the last case, however, the bromate should be run in at the rate of 90 to 100 drops a minute, with constant stirring, and, when the methyl orange begins to fade, a drop or two more of the dye added and the bromate from now on introduced a drop at a time followed by hard and thorough stirring. In this way the end point can be hit with great accuracy. If it be overstepped we can come back with the methyl orange (1 gram in a liter of water) which has been balanced against 1 or 2 drops of the bromate in 200 cc. of water containing one-fourth its volume of concentrated hydrochloric acid.

Table I. Determination of Antimony

Antimony Taken as Dihydrogen Potassium Pyro-antimoniate	Antimony Found
Gram	*Gram*
0.1067	0.1067
0.1067	0.1067
0.1067	0.1066
0.1067	0.1068
0.0854	0.0851
0.0854	0.0852
0.0427	0.0427

Convenient amounts of the standard solution were pipetted into the reductor, 15 to 20 cc. concentrated hydrochloric acid were added, and the liquid was diluted to about 75 cc. (scratch on the side of the bottle above the mercury to indicate this volume). The air in the reductor was displaced by introducing a brisk current of purified carbon dioxide gas for ten minutes, the delivery tube withdrawn, and the bottle instantly stoppered and agitated for an hour in the machine. After most of the mercurous chloride and finely divided mercury had settled (before filtering them some of the solutions stood overnight), the solution was poured on to a double filter paper (9 cm.), the filtrate being caught in a 400-cc. beaker. The slate-colored mass in the reductor was washed by letting a 10-cc. pipet full of dilute hydrochloric acid (10 cc. concentrated hydrochloric acid to 90 cc. water) flow down the inner neck and sides of the bottle, stoppering it, shaking well, decanting the liquid on to the paper, and repeating the operation five times. After rinsing off the stopper, the mouth of the reductor, and the glass rod with a little water, the mercurous chloride and mercury on the filter paper were washed until the washings were neutral. The solution was then diluted to 200 cc. and the antimony titrated. The filtration and washing require ordinarily about half an hour. The filtrates were always clear. The material on the filter paper was washed back into the reductor, the liquid, after a few minutes, poured off, and some concentrated hydrochloric acid and from 15 to 20 cc. of strong stannous chloride solution introduced. On stoppering and shaking the reductor violently for 2 or 3 minutes all the mercurous chloride is reduced to metallic mercury, which should be washed in the reductor by decantation until the washings are neutral. The reduction and washing are complete in 15 minutes. While washing the reduced mercury the author noticed a phenomenon of which he finds no mention. If, after washing is complete, the reductor be filled quite full with water, stoppered, and shaken vigorously up and down for about 15 seconds, the metal breaks up into a vast number of globules which form a foam completely filling the upper part of the bottle. The foam, however, rapidly subsides. A few milligrams of soap dissolved

in the water inhibit all tendency on the part of the metal to foam. It becomes gray in color, and must be treated again with stannous chloride to show the peculiar behavior. A little hydrochloric, sulfuric, or nitric acid in the water also precludes the mercury from foaming.

Table II. Determination of Antimony in the Presence of Arsenic Acid

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Arsenic Taken as Dihydrogen Potassium Orthoarseniate	Antimony Found
Gram	*Gram*	*Gram*
0.1067	0.0625	0.1067
0.1067	0.0625	0.1068
0.0854	0.0625	0.0851
0.0427	0.0625	0.0426

Table III. Determination of Antimony in the Presence of Arsenic and Stannic Acids

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Arsenic Taken as Dihydrogen Potassium Orthoarseniate	Tin Taken as Stannic Ammonium Chloride	Antimony Found
Gram	*Gram*	*Gram*	*Gram*
0.1067	0.0625	0.1292	0.1073
0.1067	0.0625	0.0969	0.1064
0.1067	0.0625	0.0808	0.1065
0.0854	0.0625	0.0869	0.0854
0.0854	0.0625	0.0808	0.0852
0.0427	0.0625	0.0646	0.0427

If a solution contains antimonious and arsenious acids we may determine the amount of bromate required to oxidize both, then evaporate the liquid to about 50 cc., transfer it to the reductor, reduce the antimony to the trivalent state, filter, etc., and titrate the antimony. The difference between the amounts of bromate used in the two cases gives that used to oxidize the arsenic to the quinquivalent state. Standard solution A and a 0.1 *N* solution of arsenious acid were employed.

Table IV. Determination of Both Antimony and Arsenic

Antimony Taken as Antimonious Chloride	Arsenious Oxide Taken	Antimony Found	Arsenious Oxide Found
Gram	*Gram*	*Gram*	*Gram*
0.1103	0.1237	0.1109	0.1233
0.1103	0.0990	0.1109	0.0985
0.1103	0.0495	0.1104	0.0493
0.1103[a]	0.0990	0.1103	0.0992
0.0883	0.0495	0.0885	0.0495
0.0883	0.0248	0.0885	0.0248

[a] Contained in addition 0.4 gram $(NH_4)_2SnCl_6$ = 0.1292 gram Sn.

The antimony (0.1067 gram) was determined in a solution containing roughly 0.083 gram Pb, 0.213 gram Bi, and 0.123 gram Cd, all as chlorides, and 0.1069 gram of antimony was found.

Table V. Determination of Antimony in the Presence of Copper

Antimony Taken as Dihydrogen Potassium Pyroantimoniate	Copper Taken as Crystalline Cupric Sulfate	Antimony Found
Gram	*Gram*	*Gram*
0.1067	0.0656	0.1062
0.1067	0.0656	0.1062
0.1067	0.0525	0.1064
0.1067	0.0525	0.1062
0.1067	0.0394	0.1062
0.1067	0.0262	0.1061

Cupric salts are reduced by mercury to cuprous salts, the latter being completely reconverted into the former, when a brisk current of purified air is permitted to bubble through their solutions for half an hour. Since trivalent antimony alone undergoes no perceptible change when air is passed through its solution, attempts have been made to determine quinquivalent antimony in the presence of cupric salts by reducing both, oxidizing the cuprous to the cupric with air and titrating the antimony. The results are a trifle low, a fact which may be due to the oxidation of the cuprous inducing a slight oxidation of the antimonious chloride. The determination in Table V will indicate the extent to which the results differ from the true values.

A solution (75 cc.) containing 25 cc. of concentrated HCl, 0.1067 gram of Sb as the potassium pyro-salt, 0.0625 gram of As as H_2KAsO_4, 0.037 gram of Pb, 0.086 gram of Bi, 0.059 gram of Cd, 0.057 gram of Sn^{IV}, and 0.037 gram of Cu^{II}, the last five as chlorides, was shaken with mercury for an hour in the machine, in an atmosphere of carbon dioxide. The filtrate was slightly turbid but became perfectly clear when heated to steaming and stirred a few minutes. When cool, air was passed through it for half an hour and the antimony titrated. Antimony found equaled 0.1061 gram, a result which is practically identical with the average of those given above. If to the volume of 0.1 *N* bromate used in each of the above cases 0.1 cc. be added, the calculated results are very satisfactory. Experiments are being made to determine whether or not the low results are due to the oxidation of the cuprous to the cupric salt, inducing a slight oxidation of the trivalent antimony.

Summary

Antimonic acid in hydrochloric acid solution is completely reduced to antimonious acid when the solution is shaken with mercury for an hour in an atmosphere of carbon dioxide.

Arsenic and stannic acids, as well as lead, cadmium, and bismuth, in hydrochloric solution, undergo no change when subjected to similar treatment.

In the same way cupric salts are reduced to cuprous salts, but the latter are selectively reoxidized when pure air is passed through their solutions for half an hour.

Use has been made of these facts in determining antimony in the presence of some or all the substances mentioned. In the case of copper the results are a trifle low.

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Correction. In the article on "Apparatus for Reactions in Liquid Phase at Elevated Temperatures and Pressures" [Ind. Eng. Chem., Anal. Ed., 4, 342 (1932)], the length of the tubing for the steel spiral referred to in the thirteenth line from the bottom of the first column on page 343 should have been given as 4.3 meters or 14 feet. The external diameter of the steel tubing was 6.4 mm. (0.25 inch) and the internal diameter was 1.6 mm. (0.06 inch). Homer Adkins

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Correction. In the paper on "Practical Vacuum-Tube Potentiometer for pH Measurement with Glass Electrodes" [Ind. Eng. Chem., Anal. Ed., 4, 398 (1932)] the values of certain resistors were omitted from Figure 1. R_1 is 2000 ohms, R_2 is 1000 ohms, R_3 is 50 ohms, R_4 is 500 ohms, and R_5 is 10,000 ohms. The resistor shown in the battery-charging circuit has a value of 1000 ohms; the lamp with which this resistor is in series may have a value of 10 to 75 watts (ordinary 110-volt type), depending upon individual tube-filament conditions.

Fred Rosebury

Determination of Total Dissolved Solids in Water Analysis

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THE determination of total solids is one of the oldest determinations in water analysis and has apparently always been taken to represent the amount of material in the water. The difference between the weight of the residue on evaporation of unfiltered and filtered samples of the water has sometimes been taken as a measure of the suspended matter. The loss on ignition has frequently been taken as a measure of the organic matter in the water. Comparison of reported determinations of total solids and loss on ignition with the results of analysis of the actual mineral content indicates, however, that in some analyses the figures for total solids and for loss on ignition have no real significance.

The determination of total dissolved solids is based on the weight of the residue on evaporation after drying at a temperature of 105° to 110° C. (*1*, *5*) or at 180° C. (*3*). The loss on ignition is determined on the residue used for determining total dissolved solids by careful ignition over a small flame or in a covered metal dish (*4*). In calculating the quantity of dissolved material, the figure for bicarbonate is divided by 2.03 to account for conversion to carbonate on evaporation, and the quantities of the other constituents as found by analysis are added to give the quantity of dissolved mineral matter. In most water analyses the determined figure for total dissolved solids is greater than the sum of the determined constituents, because of the retention of water of crystallization or water of occlusion and because of small quantities of undetermined constituents. In analyses of certain types of waters, however, the quantity reported for total dissolved solids is less than the sum of the determined constituents because of the volatilization of certain constituents during the evaporation and subsequent drying.

Natural waters contain varying quantities of silica and the carbonates, sulfates, chlorides, and nitrates of calcium, magnesium, sodium, and potassium. For most waters it is assumed that the silica is present in the colloidal condition and after evaporation is present as SiO_2, although in certain waters, especially some from volcanic regions, the silica in the residue is in combination with the basic elements. Natural waters can be grouped for study according to the predominating acid radicals and in this paper are discussed under four groups—carbonate, sulfate, chloride, and nitrate waters. The analyses in Table I were selected from over 5000 made in the Water Resources Laboratory of the U. S. Geological Survey to represent the different types of water.

Carbonate Waters. Natural waters of the most common type are those in which calcium and bicarbonate are the principal radicals. This type is represented by the first two analyses in Table I. The residues from certain of these waters in which magnesium is small, when dried at 180° C., represent fairly accurately the dissolved material, as shown by analysis 1. Many waters of this type, however, contain considerable magnesium, and in some of these waters the determined figure for total solids is less than the sum of the determined constituents, as shown in analysis 2. In over 1000 analyses of waters of this type the determined figure for total dissolved solids was equal to the sum of the determined constituents in 15 per cent, greater than the sum by about 4.1 parts per million in 54 per cent, and less than the sum by about 3.0 parts per million in 31 per cent. The total solids for the whole group of waters averaged 81 parts per million.

The dissolved material in another large group of waters consists chiefly of sodium and bicarbonate (*2*). This group is represented by analysis 3, which indicates that in a water of this type the determination of total solids, based on the residue dried at 180° C., agrees well with the sum of the determined constituents.

Sulfate Waters. Waters in which sulfate is present in considerable quantities yield residues on evaporation that contain sulfates of calcium, magnesium, and sodium, with water of crystallization. Most of this water is driven off from the sulfates of sodium and magnesium when the residue is heated at 180° C., but this temperature is not sufficient to dehydrate calcium sulfate completely. Waters of this type are represented by analysis 4 in Table I. A great many waters high in sulfate carry enough chloride to affect the relation between the weight of the residues and the amount of dissolved material.

Chloride Waters. Natural waters containing large quantities of chloride also generally contain considerable calcium and magnesium, and the residues from these waters are weighed with difficulty because of the presence of calcium and magnesium chlorides. The determined quantity of dissolved solids in practically all waters of this type is considerably greater than the sum of the determined constitu-

Table I. Mineral Constituents of Natural Waters

	SiO_2	Fe	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	Total Dissolved Solids at 180° C.	Sum	Fixed Residue[a]	Color
	Parts per million													
1	7.9	0.07	52	5.0	2.4	1.7	178	3.9	1.8	0.20	165	163	164	...
2	9.0	0.02	32	15	2.6	1.3	171	2.7	2.6	0.53	137	150	133	...
3	16	0.07	5.3	3.9	141	3.2	388	5.0	12	1.1	382	378	379	...
4	13	0.08	113	29	97	3.9	186	407	23	7.3	811	785	774	...
5	30	0.12	184	29	127		214	48	454	1.0	1076	979	1049	...
6	17	0.03	68	19	19	4.7	239	19	29	50	331	343	297	...
7	6.3	0.06	17	2.6	1.3	0.8	58	8.2	0.8	0.10	67	66	63	5
8	6.0	0.01	5.2	1.7	5.7	1.4	13	2.3	10	Trace	66	39	51	200

[a] Figure obtained by subtracting loss on ignition from figure for total solids.

1. Allan Springs at Price, Ala., 1928.
2. Spring at Village Springs, Ala., 1928.
3. Well, 28 feet deep, at Hendersonville, Pa., 1926.
4. San Juan River near Bluff, Utah, average, 1931.
5. Well, 162 feet deep, at St. Petersburg, Fla., 1923.
6. Well, 24 feet deep, at Bartonsville, Fla., 1931.
7. Cowpasture River at Clifton Forge, Va., 1930.
8. North Fork of Black Creek, Middleburg, Fla., 1924.

Table II. Loss of Chloride during Evaporation and Heating of Residues from Natural and Artificial Waters

	Total Dissolved Solids at 180° C.	SiO_2	Fe	Ca	Mg	Na + K	HCO_3	SO_4	Cl	NO_3	Ca	Mg	Na + K	HCO_3	SO_4	Cl	NO_3	Loss of Chloride during Evaporation and Heating 1 hr. at 180° C.
	Parts per million										Milligram equivalents							Parts per million
1	1076	30	0.12	184	29	127	214	48	454	1.0	9.2	2.4	5.5	3.5	1.0	12.8	0.0	50
2	1262	24	0.27	115	61	206	154	129	504	3.2	5.7	5.0	9.0	2.5	2.7	14.2	0.1	86
3	2630	16	0.12	177	101	643	144	253	1342	1.7	8.8	8.3	28.0	2.4	5.3	37.8	0.0	102
4	5377	8.4	0.36	254	181	1418	85	580	2662	Trace	12.7	14.9	61.6	1.4	12.1	75.1	0.0	86
5	1480	26	0.09	44	40	409	259	425	375	Trace	2.2	3.3	17.8	4.2	8.8	10.6	0.0	0
6	..	..	..	43	244	398	253	1233	366	Trace	2.1	20.0	17.3	4.1	25.7	10.3	0.0	0
7	..	..	..	37	113	340	217	353	546	Trace	1.8	9.3	14.8	3.6	7.4	14.3	0.0	0
8	..	..	..	28	192	271	174	282	720	Trace	1.4	15.8	11.8	2.9	5.9	20.3	0.0	100

1. Well, 162 feet deep, at St. Petersburg, Fla., 1923.
2. Well, 325 feet deep, at Eau Gallie, Fla., 1923.
3. Well, 265 feet deep, at Cocoa, Fla., 1923.
4. Salt Springs near Norwalk, Fla., 1924.
5. Well, 750 feet deep, at Fort Pierce, Fla., 1924.
6. Natural water to which solid magnesium sulfate was added.
7, 8. Natural waters to which a solution of magnesium chloride was added.

ents. Analysis 5 in Table I represents a water of moderate mineral content of this type.

Natural waters of the chloride type often show loss of chloride on evaporation and during the subsequent heating. The amounts of chloride in eight typical waters and the losses found after evaporation and heating are shown in Table II. In each case the loss of chloride occurred with residues from waters in which the chloride was more than equivalent to the sodium plus potassium. This was also brought out in a series of experiments with natural waters to which sodium chloride, magnesium chloride, and magnesium sulfate were added in varying amounts. The results of such an experiment with natural waters are shown by analyses 6 to 8 in Table II. It was also found that the addition of sodium sulfate or sodium carbonate to a solution of magnesium chloride in such quantities that the sodium becomes more than equivalent to the chloride eliminates the loss of chloride from such a solution.

The loss of chloride is usually not apparent from the weight of the residue on evaporation, because the amount of water held by the residue as water of crystallization is often greater than the loss of chloride.

Nitrate Waters. Most natural waters have only small quantities of nitrate. In a few, however, the nitrate is present in considerable quantities usually with considerable quantities of other constituents that affect the weight of the residue (analysis 6, Table I). Waters that contain much nitrate may lose as much as 5 or 10 parts per million of nitrate when the residue is left on the steam bath as long as 4 hours. The loss of nitrate is increased during heating at 180° C. for one hour. The losses for seven natural waters are shown in Table III.

Table III. Loss of Nitrate during Heating of Residue from Natural Waters

(Analyses made in the Water Resources Laboratory, U. S. Geological Survey)

	Total Solids at 180° C.	SiO_2	Fe	Ca	Mg	Na + K	HCO_3	SO_4	Cl	NO_3	Loss of Nitrate during Heating 4 Hours on steam bath	Loss of Nitrate during Heating 1 Hour at 180° C.
	Parts per million											
1	331	17	0.03	68	19	24	239	19	29	50	..	19
2	406[a]	..	0.10	88	35	2.2[a]	367	16	12	42	26	35
3	330[a]	..	0.21	72	17	15[a]	204	67	14	31	9	18
4	372[a]	..	..	102	18	4.6[a]	328	15	19	34	13	30
5	265[a]	..	0.05	42	26	12[a]	199	16	28	23	7	7
6	303[a]	..	0.05	70	19	11[a]	255	27	20	15	9	13
7	209[a]	..	0.04	50	15	3.5[a]	206	5	5.0	16	11	12

[a] Calculated.

1. Well, 360 feet deep, at Leesburg, Va., 1931.
2. Well, 81 feet deep, at Marlboro, Va., 1931.
3. Well, 70 feet deep, at Sudley Springs, Va., 1931.
4. Well, 122 feet deep, at White Post, Va., 1931.
5. Well, 100 feet deep, at Whitaker, Va., 1931.
6. Well, 118 feet deep, at Gainesboro, Va., 1931.
7. Well, 53 feet deep, at Goresville, Va., 1931.

Colored Waters. Natural waters are often colored by organic matter. Waters of this type are represented by analyses 7 and 8, Table I. The more highly colored water (analysis 8) showed a much greater loss on ignition than the slightly colored water, and the agreement between the total solids and the sum was better for the water having less color.

Drying and Ignition of Total Solids. Many natural waters of moderate mineral content give residues on evaporation which when weighed after drying on a steam bath, with no other heating, show a fair agreement between determined total solids and the sum of the determined constituents. For 288 waters whose residues weighed between 100 and 500 mg. the difference between the weight when dry on the steam bath and the weight after heating for an hour at 180° C. was less than 10 mg. on 166 waters, between 10 and 20 mg. on 56 waters, and more than 20 mg. on 66 waters.

More concentrated waters give residues on evaporation which may have to be dried at 180° C. for several hours to obtain a constant weight. For certain types of waters whose residues are hygroscopic and difficult to weigh, it is preferable to evaporate a suitable volume in a weighing bottle that can be stoppered during the weighing. Waters of this type can be evaporated in an open dish rather rapidly and with no appreciable loss through spattering by applying heat from a hot noncorrodible surface above the dish. The residue obtained in this manner gives a better weight for the determination of total solids than that obtained when the water is evaporated in a dish on the steam bath and the residue dried at 180° C. to constant weight, although the loss in chloride is greater when the residue is heated from above. For highly concentrated waters that contain considerable calcium, magnesium, and sodium chlorides, such as brines from oil fields, Zinzalian and Withrow (*9*) recommend drying the residues at 750° C., making a correction for the amount of calcium and magnesium chlorides in the residue on evaporation. For waters of high concentration Reistle and Lane (*6*) determined the specific gravity of a sample and used this determination as the basis of the choice of the size of sample to be analyzed. For waters whose specific gravity was greater than 1.025 the total solids were calculated from the determined specific gravity. These authors give a table for the computation of total solids from the specific gravity in a range from 1.020 (total solids, 27,500 parts per million) to 1.140 (total solids, 210,000 parts per million) and state that the total solids computed in this way should check within 2.5 per cent the determined figure for total solids, based on the residue dried at 105° C.

Relation between Conductance and Total Solids. The total salinity of irrigation waters has been estimated from the specific electric conductance of the waters by Scofield and Wilcox (*8*), who used the method recently described by Scofield (*7*) for estimating the amount of soluble salts in soils or soil solutions. These authors state:

> Where desirable, the total salt content may be estimated as parts per million from the conductance determination by the use of suitable conversion factors. For approximate estimates with irrigation waters having a conductance of 100 or more,

TABLE IV. ANALYSES AND SPECIFIC CONDUCTANCE OF DIFFERENT TYPES OF WATERS

(Analyses made in the Water Resources Laboratory, U. S. Geological Survey)

	SiO_2	Fe	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	Total Dissolved Solids at 180° C.	Sum	Specific Conductance (Reciprocal Ohms × 10^5 at 25° C.)	Sum ÷ Conductance
	Parts per million													
1	12	0.05	6.2	2.4	4.8	0.7	28	4.7	3.0	0.15	49	48	6.6	7.3
2	12	0.02	8.6	2.3	4.4	1.5	23	15	4.8	1.6	60	62	12	5.2
3	16	0.06	9.4	4.0	6.5	1.0	46	5.7	6.0	0.20	70	72	11	6.5
4	27	0.10	26	5.4	8.5	5.6	94	21	3.0	4.0	143	147	23	6.4
5	16	0.02	37	14	17	1.0	82	101	7.9	1.4	241	236	46	5.1
6	15	0.04	108	16	28	4.4	306	25	55	47	440	449	69	6.5
7	8.2	0.10	67	19	62	4.8	160	143	76	2.0	468	461	79	5.8
8	19	0.04	144	19	16	1.4	409	105	16	3.8	539	526	86	6.1
9	6.2	0.02	70	9.0	132	2.6	44	446	4.5	0.10	720	692	105	6.6
10	16	0.20	209	60	16	3.2	380	445	4.0	0.30	1018	941	120	7.8
11	8.4	0.08	100	44	217	4.0	222	372	231	14	1139	1100	185	5.9
12	16	0.10	120	60	129	3.7	195	599	22	15	1129	1061	146	7.3

1. Sacramento River at Sacramento, Calif., April 20, 1932.
2. Northwest Branch at Takoma Park, Md., April 18, 1932.
3. Sacramento River at Sacramento, Calif., April 6, 1932.
4. Well, 704 feet deep, at Middleburg, Va., October 30, 1931.
5. Canoe Brook at Irvington, N. J., February 26, 1932.
6. Well, 300 feet deep, at Berryville, Va., October 29, 1931
7. Dolores River near Cisco, Utah, April 1, 1932.
8. Well, 95 feet deep, at Stephens City, Va., October 28, 1931.
9. Wells at Marion, Ohio, part of public supply, treated water, April 6, 1932.
10. Wells at Marion, Ohio, part of public supply, raw water, April 6, 1932.
11. Colorado River near Grand Junction, Colo., March 11 to 20, 1932.
12. Gunnison River near Grand Junction, Colo., March 11 to 20, 1932.

in which sulfates predominate, the conductance multiplied by 7 will give a figure fairly close to the total salt content in parts per million. If the conductance is much below 100 or if chlorides predominate in the salt complex, then the conductance multiplied by 6 will be nearer the true value for total salt content.

Natural waters of different types give inconsistent results when an attempt is made to determine the factor that should be used to estimate the amount of dissolved material from the specific conductance. This was pointed out by Scofield (7) and is shown by typical results given in Table IV. The factor that must be used to obtain the quantity of dissolved solids from the conductivity of these 12 waters ranges from 5.1 to 7.8 and is not consistent for any range of solids or any type of water. Analyses 10 and 9, which have quite different conversion factors for estimating the solids from the conductivity, represent the raw and treated water of a public supply. Analyses 11 and 12, also with quite different factors, represent waters of similar quantities of dissolved solids but different in nature. It is evident that the conductivity is not an accurate measure of the dissolved solids, though it may serve to give approximate results of some practical value.

SUMMARY

The figure for total dissolved solids, based on the weight of the residue on evaporation after heating for 1 hour at 180° C., is reasonably close to the sum of the determined constituents for most natural waters.

Waters of the carbonate type that are high in magnesium may give residues that weigh less than the sum. Natural waters of the sulfate type usually give residues that are too high on account of incomplete drying.

Residues from waters high in chloride, in which the chloride is more than equivalent to the alkalies, may lose from 50 to 100 parts per million of chloride on heating. Residues from water high in nitrate may lose as much as 30 parts of nitrate on heating.

Waters of high concentration give more consistent results for the total dissolved solids when a small volume is evaporated in a weighing bottle. Time may be saved by evaporation in a dish by application of heat from above.

The specific conductivity of a water may be used to calculate approximately the quantity of dissolved material if the nature of the dissolved material is known.

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An Inexpensive Flame Shield

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A NUMBER of excellent flame shields are available from the various scientific supply houses at fairly low prices, but even this low cost assumes importance when a relatively large number of students must be supplied. Then, too, in research laboratories, the investigator often needs a flame shield immediately and is inconvenienced if it must be ordered. For these reasons the device described in this article is worth consideration.

The construction of the device is extremely simple. A tin can of the size used for prepared soups is secured, the top cut off smoothly, and a hole punched in the bottom. This hole should be of a size such that it fits tightly the upright tube of the burner, on which the shield is to be used. Adjustment is secured by raising or lowering the can, friction maintaining the position if the hole is of the proper size.

Larger cans may be used if a larger shield be desired. In some cases, gallon cans with both the top and bottom removed and holes punched in the sides for air inlets are advantageous. The relatively short life of the device is compensated by its inexpensiveness.

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Volumetric Method for Determination of Fluorine

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A method is described for titrating soluble fluoride and silico-fluoride solutions with standard thorium nitrate, using a zirconium-alizarin mixture as indicator. A method for the volatilization of fluorine as hydrofluosilicic acid and the titration of the fluorine in the distillate gives theoretical results in the absence of a large amount of gelatinous silica. Materials which cannot be decomposed by perchloric acid must be fused with sodium carbonate before the fluorine can be volatilized as hydrofluosilicic acid. A method is described for removing the silica when a sufficient amount is present to interfere with the volatilization of the fluorine. Volatilization of fluorine as silicon tetrafluoride from certain insoluble fluorides and determination of the fluorine by titration with thorium nitrate was found to give unsatisfactory results in the presence of plant ash. An attempt was made to volatilize fluorine quantitatively as hydrofluoboric acid and titrate the fluorine in the distillate but the results were inconsistent.

Many methods have been devised for the determination of fluorine. All these are rather long and tedious, and none is satisfactory for the determination of this element in all kinds of materials. Since it has been found that fluorine plays a much more important role in metabolic processes than was formerly believed, and since materials containing it are now being used extensively in commercial products, such as insecticides and mineral supplements in feeds, a short accurate method for its determination is needed.

Since bibliographies (*1, 16*) are found in the literature, only those methods which have a direct bearing on the technic to be described will be mentioned here. Deladrier (*5*), Pisani (*12*), and others determined the fluorine in soluble fluorides by precipitation as thorium fluoride. They ignited the precipitate to the oxide under suitable conditions and calculated the amount of fluorine present. Gooch and Kobayashi (*7*) used the same method, and also made a preliminary report on dissolving and titrating the thorium fluoride. DeBoer (*4*) and others, and later Pavelka (*11*), Feigl (*6*), and Alamarin (*2*), determined fluorine colorimetrically by the use of a zirconium-alizarin mixture, the color of which faded in the presence of fluorine.

Wöhler (*19*), Offermann (*10*), Wagner and Ross (*18*), Reynolds, Ross, and Jacob (*14*), Reynolds and Jacob (*13*), Shuey (*17*), and others determined the fluorine in certain insoluble fluorides by the volatilization method. They decomposed the material by means of silica and sulfuric acid in a perfectly dry atmosphere, collected the silicon tetrafluoride gas in water or other solvent, and determined the soluble fluoride by one of the many methods found in the literature. This method in general has been found tedious and not very satisfactory. Casares (*3*) modified it by using finely ground glass instead of pure silica, and claimed a quantitative evolution of the silicon tetrafluoride in a few minutes when heated at a temperature of 160° C.

Schrenk and Ode (*15*) determined silica in substances containing fluorine by volatilizing the fluorine as boron trifluoride or hydrofluoboric acid. This was done by treating the materials with boric acid and hydrochloric, perchloric, or sulfuric acid, and evaporating.

In developing a method by which small quantities of fluorine could be determined in soluble fluorides, an attempt was made to use the colorimetric method based upon a zirconium-alizarin mixture. With this procedure, however, the fluorine content was not proportional to the fading of color, and the results were not sufficiently consistent to plot a curve that would show any definite relationship between the two. It was noted, however, that when an extremely dilute solution of a fluoride was added to a small amount of the dye, the color faded very slowly until the end point of the formation of a zirconium fluorine complex was reached, and then the dye decolorized quite suddenly. This indicated the possibility of using the dye as an indicator to show when the precipitation of fluoride was complete. Since thorium fluoride is quite insoluble in a solution containing ethyl alcohol, an attempt was made to titrate fluoride solutions containing an equal volume of ethyl alcohol with standard thorium nitrate, using the zirconium-alizarin mixture to determine the point at which all of the fluorine was precipitated. The results with pure fluoride solutions were good.

Determination in Soluble Fluorides

With No Interfering Elements[1] Present. The reagents used for determining fluorine in solution when no interfering elements are present are as follows: (1) Zirconium nitrate, 1 gram of $Zr(NO_3)_4 5H_2O$ in 250 cc. of water. (2) Alizarin red, 1 gram of sodium alizarin sulfonate in 100 cc. of ethyl alcohol. Filter off the undissolved residue and add 150 cc. of ethyl alcohol to the filtrate. The two solutions are kept in stock and mixed, three parts of (1) and two parts of (2) as needed. The color should be violet-red when mixed. (3) Thorium nitrate solution, standardized against a known fluoride solution. (4) Standard fluoride solution, lithium fluoride, 0.02 *N* solution or specially purified sodium fluoride of the desired concentration. (5) Hydrochloric acid, approximately 1 to 50.

Dissolve a weighed quantity of the fluoride in water and make up to a given volume. Transfer an aliquot of the solution to be analyzed to a small tall-form beaker, add water to make a volume of approximately 20 cc. and 3 drops of the zirconium-alizarin mixture.[2] If necessary, add just enough

[1] Any ion which forms a precipitate or a nondissociated salt with fluorine or with thorium interferes with the titration—e. g., Ca^{++}, Ba^{++}, Fe^{+++}, Al^{+++}, PO_4^{---}, etc.

[2] If the volume of the solution to be titrated is sufficiently small (4 to 8 cc.) so that the color can be distinguished, the accuracy of the titration is increased by using only one drop of the indicator. If the volume is large, it may be necessary to add more than 3 drops (50 to 75 cc. require 6 drops). For very accurate results it is necessary to standardize the thorium nitrate in approximately the same volume and with the same number of drops of indicator as the unknown, and titrate the two to the same color. The

dilute hydrochloric acid to destroy the color. Add an equal volume of neutral ethyl alcohol, and titrate over a white surface in good light with the standard thorium nitrate to a faint permanent reappearance of color. The reaction is slow near the end point. When titrating with 0.01 *N* thorium nitrate, make a correction for the fluorine which combines with the indicator. Determine this by titrating the number of drops of indicator used in the titration with 0.01 *N* fluoride solution to the disappearance of the color.

In order to determine the sensitivity of the method, 0.1 and 0.01 *N* solutions of thorium nitrate and solutions of sodium fluoride were prepared, and the latter were titrated with the former, using 3 drops of the zirconium-alizarin mixture as the indicator. Furthermore, four synthetic solutions (numbers 1, 2, 3, and 4) of known fluorine content were prepared. The fluorine in each of these was determined by two analysts, A and B, who did not know the fluorine content of the solutions. The results of the titration of the known fluoride solutions are found in Table I, and those of the synthetic solutions in Table II.

Table I. Titration of Fluoride Solutions with Standard Thorium Nitrate

Thorium Nitrate Normality	Thorium Nitrate Amt.	F Present	F Found	Error
	Cc.	*Mg.*	*Mg.*	*Mg.*
0.1	0.81	1.54	1.54	+0.00
	0 79		1.50	−0.04
	1.64	3.08	3.12	+0.04
	1.60		3.04	−0.04
	2.39	4.62	4.55	−0.07
	2.35		4.47	−0.15
	3.93	7.70	7.47	−0.23
	3.95		7.52	−0.18
	8.00	15.40	15.20	−0.20
	7.99		15.18	−0.22
0.01	0.80[a]	0.154	0.152	−0.002
	0.79		0.150	−0.004
	1.61	0.308	0.306	−0.002
	1.61		0.306	−0.002
	2.42	0.462	0.460	−0.002
	2.39		0.454	−0.008
	3.85	0.770	0.732	−0.038
	8.04	1.540	1.528	−0.026
	7.90		1.501	−0.039

[a] 0.30 cc. of sodium fluoride was necessary to decolorize indicator. Therefore, this was added as correction to thorium nitrate required.

The data in Table I show that the maximum difference in duplicate titrations is 0.08 mg. of fluorine when titrating with 0.1 *N* thorium nitrate solution, and 0.003 mg. of fluorine when titrating with 0.01 *N* solution. Similar results were obtained when sodium silicofluoride was titrated with thorium nitrate.

Table II. Fluorine in Unknown Synthetic Solutions

Soln.	F Present	F Found By A	F Found By B
	Mg.	*Mg.*	*Mg.*
1	4.62	4.57 4.53	4.46
2	0.913	0.926 0.918	0.905
3	0.230	0.236 0.231	0.240
4	0.137	0.137 0.134	0.136

The maximum error in Table II is approximately 4 per cent. This undoubtedly is as low as can be expected when determining such small quantities of fluorine.

With Interfering Elements Present. When interfering elements are present in the soluble fluoride solutions, the fluorine must be separated from the other elements before the titrations can be made. This may be done by volatilizing it as hydrofluosilicic acid by simply adding perchloric or sulfuric acid (perchloric acid is preferable since nearly all of the perchlorates are very soluble), water, and several pieces of glass to the sample in a distillation flask, and distilling. When only a small quantity of fluorine (10 mg. or less) is present in the sample and the temperature is not allowed to rise above approximately 125° C., the pieces of glass appear to supply the silica necessary to combine with the fluorine to form hydrofluosilicic acid, and there is no noticeable etching of the flask. If there is more fluorine present or the temperature is allowed to rise higher, silica is taken from the flask, and etching is noticeable. In either case, however, the fluorine is recovered quantitatively.

Table III. Volatilization of Fluorine as Hydrofluosilicic Acid

Material	Distillate	F Present	F Found
	Cc.	*Mg.*	*Mg.*
NaF soln.	50	7.37	7.37
NaF soln.	50	7.37	7.43
NaF soln.	30[a]	0.167	0.167
NaF soln. + plant ash	50	7.37	7.37
NaF soln. + plant ash	50	7.37	7.40
NaF soln. + plant ash	30[a]	0.167	0.171
NaF soln. + plant ash	30	0.017	0.019
NaF soln. + 100 mg. of gelatinous silica	50	9.73	8.96
NaF soln. + 100 mg. of gelatinous silica	100	9.73	9.27
NaF soln. + 100 mg. of gelatinous silica	150	9.73	9.73
NaF soln. + 50 mg. of gelatinous silica	50	9.73	9.64
NaF soln. + 100 mg. of boric acid	150	9.73	9.68
NaF soln. + 20 mg. boric acid	100	9.73	9.80
NaF soln. + 1000 mg. $AlCl_3$	250	9.50	5.14
NaF soln. + 250 mg. $AlCl_3$	225	9.50	9.34
NaF soln. + 100 mg. $AlCl_3$	50	9.50	9.47
NaF soln. + 50 mg. $AlCl_3$	50	9.50	9.45
Na_2SiF	50	7.54	7.51

[a] Concentrated to 15 cc. before titration and 3 drops of indicator used.

The following procedure was used for determining fluorine under the above conditions: Place the sample in a small distillation flask, and add a few glass beads or pieces of porous plate, 5 cc. of 60 per cent perchloric acid, and sufficient water to cause the solution to boil at 110° C. or less. Place the flask on an asbestos mat with an opening large enough so that about one-third of the flask will be exposed to the flame. Close with a two-hole rubber stopper through which passes a thermometer and a capillary tube, both of which extend down into the liquid. Connect a dropping funnel with the capillary tube so that water may be added during the process of distillation, and fill this with water. Connect the flask with a water condenser. The distillate may be collected in an open container. Distil until the boiling point of the solution reaches 135° C.[3] and hold at approximately that temperature by allowing water to run into the flask from a dropping funnel, until all of the fluorine has been volatilized. This is usually accomplished by distilling over 50 to 75 cc. Add 6 drops of the zirconium-alizarin mixture and dilute sodium hydroxide drop by drop until the color of the indicator appears. Add an equal volume of ethyl alcohol and then dilute acid until the color of the indicator just disappears (at this point it is advisable to cause the color to appear and disappear two or three times to be sure to have the solution only very slightly acid). Titrate with thorium nitrate as previously directed under the determination of soluble fluorides.

Boric acid or gelatinous silica retards the volatilization. When these are present, more distillate must be collected. (If the volume of the distillate is much more than 75 cc., it is advisable to make slightly alkaline to a piece of litmus paper with sodium hydroxide and concentrate to that volume or less.) The presence of a very large quantity of aluminum salts interferes with the volatilization of the fluorine, but no sample was found where there was a sufficient amount of these salts present to cause any difficulty.

end point is not sharp in the presence of a large amount of thorium fluoride; not more than 10 cc. of 0.1 *N* thorium nitrate should be used for the titration.

Quinalizarin (1·2·5·8 hydroxyanthraquinone) forms a lake with thorium. A few preliminary titrations indicated that this dye might be used instead of the zirconium-alizarin mixture for determining the end point of the titration.

[3] Quantitative recovery of fluorine was obtained with the temperature anywhere between 120° and 150° C. However, when a large amount of organic material is present, care should be taken to prevent the temperature from rising above 135° C., as otherwise an oxidizing action may occur which is unduly violent. In such cases sulfuric acid may be preferable.

Table III gives the results of several fluorine determinations both in the presence and absence of boric acid, silica, or aluminum salts. The volume of distillate shown was collected after the temperature had reached 135° C.

The data in Table III show that all the fluorine was readily volatilized in all cases where no gelatinous silica or boric acid was present, and that as small a quantity as 0.019 mg. of fluorine was accurately determined. It should be stated that this amount was easily determined accurately and that it is not the lower limit of the method. In the cases where a small quantity of silica gel or boric acid was present, quantitative results were obtained by prolonging the distillation. The presence of a small quantity of aluminum did not interfere.

Determination in Insoluble Fluorides after Volatilization of Fluorine as Hydrofluosilicic Acid

Insoluble fluorides which can be decomposed by perchloric acid at the concentration used in the above procedure may be placed in the distillation flask and the fluorine determined as previously described. Table IV gives the results of the determinations of fluorine in a number of insoluble fluorides which are decomposed by perchloric acid. This table includes rock phosphate, a phosphatic calcareous material which cannot be brought into the water-soluble condition by a single fusion with alkaline fluxes (*13*); cryolite, which contains a high percentage of aluminum; and a feed to which a known quantity of fluorine had been added.

Table IV. Fluorine in Insoluble Fluorides Decomposed by Perchloric Acid

Sample	Material	F Found	F Present	F Found
Mg.		*Mg.*	%	%
50	Fluorite	24.45	48.70[a]	48.90
50	Fluorite	24.24	48.70[a]	48.48
250	Apatite	9.78	...	3.91
250	Apatite	9.83	...	3.93
250	Rock phosphate	8.68	3.52[b]	3.47
250	Rock phosphate	8.75	3.52[b]	3.50
250	Rock phosphate + plant ash	8.89	3.52[b]	3.56
250	Rock phosphate + plant ash	8.84	3.52[b]	3.54
250	Rock phosphate + feed $Ca(OH)_2$ burned (*1*)	8 61	3.52[b]	3.44
250	Rock phosphate + feed $Ca(OH)_2$ burned (*1*)	8.75	3.52[b]	3.50
50	Cryolite	27.09	54.20[c]	54.18
50	Cryolite	27.18	...	54.36

[a] Theoretical.
[b] B. S Sample 56. Reported by Jacob and Reynolds (*9*).
[c] From Pennsylvania Salt Mfg. Co., Philadelphia. Reported in personal etter.

Opal glass could not be decomposed by means of perchloric acid. This material was fused with five times its weight of sodium carbonate, and the mass was taken up with a small amount of hot water. (Some materials may require more than five times their weight of sodium carbonate for complete fusion.) When only a small sample was taken so that the amount of silica present was low, the material was transferred to the distillation flask by means of a fine jet of water, neutralized with perchloric acid, an excess of 5 to 8 cc. of perchloric acid was added, and the sample was distilled in the usual way. When a large amount of silica was present, the following procedure (*8*) was followed: Fuse 0.5 gram of the sample with 2.5 grams of sodium carbonate, leach the mass with hot water, filter, and wash. Transfer the insoluble residue back to the dish in which it was leached by means of a fine jet with about 50 cc. of hot water, add sodium carbonate to make approximately a 2 per cent solution, boil a few minutes, filter, and wash thoroughly with hot water. To the combined filtrates which should have a volume of 300 cc., add 0.5 gram of zinc oxide dissolved in perchloric acid, boil the alkaline solution for one minute, filter, and wash with hot water. Concentrate the filtrate to 200 cc., add a drop of methyl red, neutralize to a very faint pink with dilute perchloric acid, add a solution of 0.25 gram of zinc oxide and 0.5 gram of ammonium carbonate dissolved in 0.5 cc. of ammonium hydroxide and 10 cc. of water. (Place on steam bath until a clear solution is obtained.) Boil the solution until the odor of ammonia has entirely disappeared, concentrate to about 100 cc., filter, and wash with cold water. Concentrate the filtrate to 25 cc., and either transfer to the distillation flask for the determination of fluorine; or to a 50-cc. volumetric flask, make up to volume, and take an aliquot for the determination.

Bureau of Standards standard sample 91 (opal glass) was taken as a typical material which could not be decomposed by means of dilute perchloric acid. This was run by the method described in the preceding two paragraphs. The results of these determinations are given in Table V.

Table V. Fluorine in Opal Glass

Sample	Condition of Sample	F Present	F Found
Mg.		%	%
100	Without fusion	5.72	1.51
100	Fused, silica present	5.72	5.63
100	Fused, silica present	5.72	5.60
100	Fused, silica present	5.72	5.78
200	Fused, silica present	5.72	5.48
100	Fused, silica removed	5.72	5.71
100	Fused, silica removed	5.72	5.76
200	Fused, silica removed	5.72	5.66
200	Fused, silica removed	5.72	5.68

The results in Table V show that if opal glass is fused with sodium carbonate the fluorine can be volatilized quantitatively. When considerable silica is present, it separates on boiling, and a gelatinous mass is formed which sometimes is difficult to keep washed down from the wall of the flask by shaking. This causes low results. In such cases the silica must be removed as previously described.

Opal glass is a representative sample of materials which cannot be decomposed by digesting with perchloric acid and of those which contain a high percentage of silica. Apatite and rock phosphate are representative samples of phosphatic materials from which fluorine cannot easily be recovered by fusion (*13*), but which are soluble in perchloric acid. Hence, since fluorine can be accurately determined in these materials, it appears safe to assume that the method should be applicable to all kinds of materials. Furthermore, only a few materials will require fusion, and from only a very few of these will it be necessary to remove the silica.

The method for the determination of fluorine which is described above is short and accurate, and the apparatus is simple and easy to manipulate. The zirconium-alizarin mixture used as the indicator is apparently almost specific for the fluoride ion. The volatilization of fluorine as hydrofluosilicic acid may be carried out over a comparatively wide range of temperature and in the presence of water. Hence, no special precautions are necessary. It should prove to be a very practical method.

Volatilization as Silicon Tetrafluoride. In order to compare the method just described with the old method of volatilization as silicon tetrafluoride, the procedure of Casares (*3*) was followed, and the fluoride volatilized was titrated with thorium nitrate. This method is much less convenient than the new one, and does not give a quantitative recovery with certain materials, as will be shown below.

The following substances were analyzed as representative samples of inorganic insoluble fluorides which can be decomposed with silica and sulfuric acid: c. p. sodium silicofluoride, a perfect crystal of colorless fluorite, c. p. calcium fluoride, and Tennessee phosphate rock (Bureau of Standards sample 56). The results are shown in Table VI.

Table VI. Fluorine in Insoluble Fluorides after Volatilization as SiF_4

Material	F Present	F Found
	%	%
Sodium silicofluoride, c. p.	60.37[a]	60.09
Fluorite	48.68[a]	48.68
		48.67
Calcium fluoride, c. p.	48.05[a]	48.12
		48.32
Rock phosphate	3.52[b]	3.55
		3.40
		3.48
		3.29
		3.49
		3.54
		3.44

[a] Theoretical corrected for moisture.
[b] Reported by Jacob and Reynolds (*9*).

The data in Table VI show that the fluorine can be recovered quantitatively from these fluorides by the old method. It cannot, however, be recovered from all types of mixtures, especially the ash of feeds.

Ordinary feeds undoubtedly contain very little fluorine. Since none could be found in 5-gram samples, it appeared advisable to add some material containing a known quantity of fluorine to a feed, burn the mixture after incorporating a suspension of calcium hydroxide, and determine whether or not the fluorine could be recovered. It was not recovered quantitatively. The next step was to add rock phosphate and fluorite, the fluorine content of which is given in Table VI, to the ash after burning the feed. The data showing the recovery when the fluoride was added to the ash are found in Table VII.

Table VII. Analysis of Feeds to Ash of Which Fluorine Had Been Added

(SiF_4 method)

Sample	Material Added	Feed Ashed	Present	Found
		Grams	*Mg.*	*Mg.*
1	Rock phosphate	5	8.81	7.35
2	Rock phosphate	3		8.03
3	Fluorite	5	12.17	10.71
4	Fluorite	3		11.71

It will be noted from the results in Table VII that the fluorine was not all recovered. Furthermore, these as well as other results not reported indicate that the percentage of loss was independent of the quantity of fluoride material added, but increased with an increase in the amount of ash taken. Since the materials added to the ash in obtaining these data were those from which the fluorine was completely volatilized (Table VI) when not in the presence of the ash, the results appear to indicate that something in the ash prevents the volatilization of fluorine as silicon tetrafluoride. This may be in accordance with the conclusion drawn by Reynolds and Jacob (*13*) who claim that in the presence of silicates part of the fluorine combines to form a nonvolatile silicon oxyfluoride. That this difficulty is overcome when the fluorine is volatilized as hydrofluosilicic acid is shown in Table IV.

Volatilization as Hydrofluoboric Acid. The method of Schrenk and Ode (*15*) for the determination of silica in materials containing fluorine suggested the possibility of volatilizing fluorine from its compounds as hydrofluoboric acid, collecting the distillate, and titrating the fluorine with standard thorium nitrate. This was carried out by placing the sample, together with water, boric acid, and either perchloric or sulfuric acid, in a Pyrex distillation flask and distilling the mixture until the temperature reached the boiling point of the acid used. The mixture was then allowed to cool, more water was added, and the distillation repeated. The distillate was neutralized, made slightly acid, and titrated with standard thorium nitrate. Even though more water was added, the distillation was repeated several times, and the time of distillation, temperature, amounts of reagents used, etc., were varied in this procedure, the results were very erratic. In only a few of the determinations did the fluorine recovered approximate the theoretical amount present. Sulfuric acid gave better results than perchloric.

After considerable work had been done on the method, it was learned that when the temperature was kept low by adding water during the distillation, the fluorine could sometimes be recovered quantitatively, provided the distillation was continued long enough (sometimes 200 to 250 cc. of distillate were collected). However, for some unexplained reason, this could not always be done. When several determinations were run as nearly alike as possible, the results varied considerably and no single combination of factors could be found which always gave theoretical results.

Table VIII gives the results of several determinations made under conditions which appeared to be as good as any that could be found. In this, one gram of boric acid, 10 cc. of sulfuric acid (1 to 1), and water were added to the sample and the temperature was not allowed to rise above 130° C. during the distillation.

Table VIII. Volatilization of Fluorine as Hydrofluoboric Acid

F Present	F Found
Mg.	*Mg.*
4.20	4.20
4.20	3.42
4.20	3.50
4.20	3.62
4.20	4.10
4.20	3.30
4.20	3.34
4.20	4.02

It is obvious that these results are not consistent. However, it appears possible that if proper conditions could be maintained, the method might prove satisfactory.

Acknowledgment

The authors are indebted to Miss Lillian Butler, Michigan Agricultural Experiment Station, for assistance in making some of the determinations.

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Determination of Moisture in Sirups and Viscous Materials

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A MORE satisfactory method for moisture than is at present in general use is needed for substances which are difficult to dry without some decomposition of the material itself. Because the determination of water in sirups and honeys by a drying process or by distillation seems always to be accompanied by decomposition, attaining a constant weight is impossible (*2*). This laboratory has been searching for a better method and has tried out all which have come to notice. This long search has been rewarded through the development of a method which does produce a dry condition in viscous material in a very short time and with comparative ease of manipulation.

The authors have hesitated to publish this paper because of a possibility that the water of crystallization of dextrose might not be driven off at 70° C. in a vacuum oven. This point has been cleared up in a report by R. T. Balch (*1*), wherein authorities are quoted to indicate that the water is driven off at that temperature. It was conceived as possible that a small amount of sample could be placed between two transparent sheets which could then be subjected to the action of a roller to spread the sample over the inner surfaces to such an extent that the film left when the two sheets were pulled apart would be thin enough to dry rapidly. An attempt was made to use celluloid and then Cellophane, but the natural moisture content made these materials useless. Some pieces of best quality mica were then tried with good results for a time, but the repeated rolling tended to cause the layers of the material to separate, and when the plates were washed following a determination, the water was drawn into the interior of the mica through capillarity, and it required long drying to remove it completely. It was also found that the continued rolling caused small flakes of mica to peel off, and unless very careful watch was kept, sudden changes in weight would result. An attempt was made to cover the plates with a thin coating of lacquer, and finally to seal and bind the edges together, but this was found unsatisfactory because the lacquer became either sticky or brittle.

Some sudden variations of 0.1 to 0.2 per cent of the original weight taken sometimes occurred and would remain constant. Results were checked by running clean plates at the same time as the plates used for the determination, and also by recording the relative humidity whenever drying was attempted or weights were made, but no reason could be found for the variations. Thin plates of shim brass of 0.003 inch (0.0007 cm.) thickness were being used, and finally it was discovered that by rubbing one of these plates with a towel one could remove enough oxide from the surface to reduce the weight by 14 mg. It was also found that if the plates covered with the sirup were not held tightly together during weighing, enough moisture could be absorbed from the air in a few seconds to cause a rise of 0.2 per cent in the weight of sample taken. Plates were then obtained of other metals, and a weighing frame was made from aluminum to hold the plates closely together with the sample inside, thus to prevent the air from having free access to the used surfaces of the plates. Application of this new method was made in determining the moisture in a sample of honey and in samples of invert sugar, in addition to many tests on blackstrap and sirups. Various determinations were made by the official A. O. A. C. sand method, and then upon metal plates with results as shown in the accompanying table.

A total of 110 determinations was made, in some cases to 33 hours' total drying time, and as data were accumulated various modifications were adopted to simplify and shorten the method. The most difficult substance to dry was commercial glucose, and it was finally discovered that the trouble, which was mechanical loss through the flaking off of the partly dry material, could be overcome by a more thorough rolling out upon the plate. The authors are convinced that any of the substances already mentioned can be dried satisfactorily in 2 to 4 hours in a vacuum oven at 70° C.

Method. Two silver plates 10 by 15 cm. and 0.003 inch (0.0007 cm.) in thickness are cut with rounding corners and provided with a light skeleton frame of aluminum. One plate is laid on the table and a drop of sample of about 0.25 to 0.3 gram placed about 5 cm. from one end. The plates are then placed together with the sample between and rolled toward the far end a few times to make them stick together. They are then placed in the frame and weighed to obtain the weight of the sample taken. They are taken out of the frame and placed upon a piece of warm (60° to 70° C.) plate glass and rolled with a rubber-faced roller, such as is used to mount photographs, to maximum distribution, and then finished off with a wooden roll whereby considerably more spreading can be attained. With a little practice a proper spread should not require over 2 to 3 minutes. It is possible to

Table I

Hours drying:	2	3	4	5	6	7	8	9	10	12
Honey, 16.50%[a]	16.04	16.06	...	16.06	...	16.10	...	16.10	...	...
Bx 80.5 invert	17.47	...	17.56	...	17.44	...	17.50	...	...	17.53
Bx 74.52 invert, av. of 3 tests	...	...	23.41	...	23.74	...	23.94	...	23.94	24.00
Blackstrap 21.78 No. 2[a]	...	21.12	...	21.49	...	21.49	...	21.52	21.61	21.58
Blackstrap 21.03 No. 1[a]	20.37	20.63	20.74	20.88	21.04	21.36	21.50	...	21.72	21.90
Filtered sirup 20.40%[a]	19.68	...	19.88	...	19.98	...	19.98	...	20.00	...
Second test	19.95	...	20.16	...	20.21	20.21	...	20.21	...	...
Third test	19.73	19.93	...	...	...	20.04	...	20.07	...	...
Filtered sirups 20.91%[a]	20.31	...	20.48	...	20.55	...	20.60	...	20.63	20.48

[a] Moisture by A. O. A. C. sand method.

Results attained up to this point clearly indicated great possibilities if the proper thin plates could be obtained, and it was finally decided that thin metal plates might be used if care were taken in the rolling so that none of the sample was allowed to approach too near the edges. A very satisfactory distribution was obtained by placing a 0.3-gram sample near one end of one plate and, after the plates were placed together, rolling them in a small clothes wringer. Results immediately became concordant and consistent, and it was found that 2 hours in a vacuum drying oven at 70° C. gave a constant weight, and additional drying could be continued for 30 hours without further material loss in weight.

feel the material push ahead of the wooden roll, and the proper spread can be accomplished without separating the plates. It is advisable to separate them partly to check the spread until one becomes accustomed to the method. The rubber roll should be longer than the plates are wide, and the wooden roll 1 to 2 inches (2.5 to 5 cm.) in length. The wooden roll must be used only after the rubber roll or the plates will begin to dish. Results indicate that if constant weight is not attained in 2 to 4 hours, the rolling was not sufficient. When no further spreading is possible, the plates are pulled apart and placed in the drying oven. When it is necessary to weigh, they must be placed together as quickly as possible with the sample side in, and slipped into the frame and cooled in a desiccator. Cooling as well as heating is very quick. The final most satisfactory equipment was obtained from Eimer & Amend.

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Photographic Recording of Line Tests for Vitamin D

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Stevens and Nelson (*1*) have recently reported a method developed in their laboratory for keeping permanent records of vitamin D line tests. For the last four years a photographic method, developed independently of theirs and depending on the same general principles, but differing in a number of details, has been used in this laboratory. The possibility that some workers may find these alternative methods better adapted to their conditions than are those of Stevens and Nelson led to the publishing of this report. As a matter of convenience, the stages of procedure will be described in chronological order.

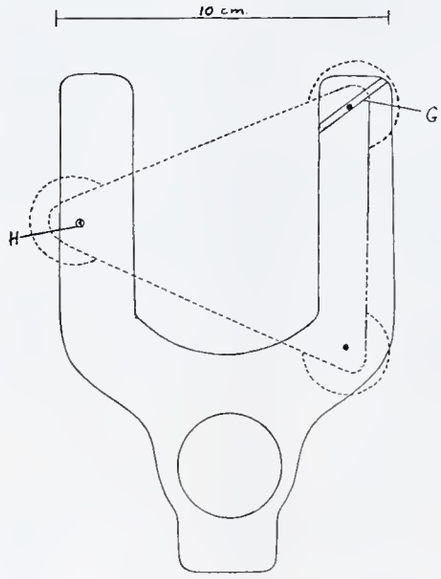


Figure 1. Plan of Microscope Stand

H, hole, and *G*, groove, for receiving feet of triangular platform; outline of triangular platform and leveling screws in place shown by dotted lines.

Preparation of Bone

As it is sometimes necessary to keep the bones for a few days before they are stained, as, for example, when several animals are being taken off one test on different days, the cleaned, unsplit bone is simply dropped into neutralized 10 per cent formaldehyde solution until it is wanted for further treatment. Bones cleaned of blood in this way with formalin give somewhat clearer lines than those cleaned with alcohol.

Owing to the frequent shortage of bright sunlight in London, bones are usually stained at about 12 inches (30.5 cm.) from a Hanovia 220-volt mercury arc for a period of about 60 seconds. After being washed, the bones are "fixed" for a few moments in 25 per cent sodium thiosulfate solution. This seems to make the staining more permanent, and is a convenience if photography is to be postponed for some days. The process must, however, be watched, as too prolonged a treatment tends to "unstain" the bones. Figures 4 and 5 are of bones that had been stained and "fixed" 4 weeks before. In other respects this treatment of the bones is essentially the same as that used by various other workers.

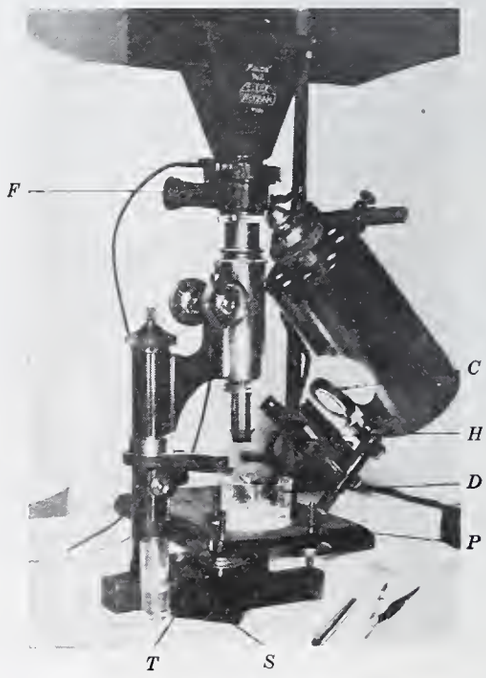
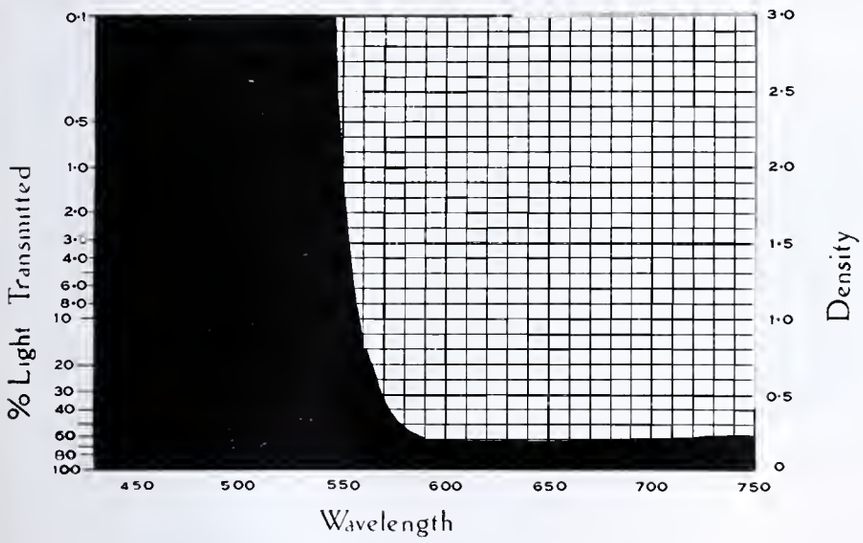


Figure 2. Photomicrographic Set

F, focusing eye-piece
C, condenser for "Pointolite" lamp
H, holder for color screen
D, glass dish for holding specimen
P, paper record of animal number
S, color screen (not in place)
T, triangular platform with leveling screws

The Optical System

An ordinary Zeiss microscope stand, with coarse and fine adjustment, a Watson "Holos" 3-inch (7.6-cm.) objective, and a Leitz Periplan O. K. six-times eyepiece are used. Instead of fitting the objective to the lower end of the draw-tube, as do Stevens and Nelson, it seems best to remove the whole of the microscope stage and place the specimen to be photographed either on the bench, or on a little triangular platform fitted with an adjustable leveling screw at each corner. One of these screws fits into a small hole on one side of the microscope foot, the other into a groove on the other; the third foot is apparently free, but actually has no degrees of freedom, and the platform is therefore quite firm during focusing and exposure (see Figure 1).



Courtesy Messrs. Ilford, Ltd., England

Figure 3. "Ilford" Micro Filter No. 5 Transmission Curve

The camera attachment by Leitz has a side-focusing ocular, but unfortunately this can be used only as a "spy-hole," to verify the position of the specimen and the illuminated circle in the microscope field, and not for actual focusing, which must be done on the ground-glass screen of the camera. Owing to certain optical effects, the image given by the ocular appears sharp over a much greater range of the microscope adjustments than does the image of the screen. The manufacturers have informed the authors that this trouble is inherent in the use of the camera for low magnifications. The accommodation of the eye adjusts automatically for minor errors in focusing by the ocular, whereas these errors can be detected on the ground-glass screen. The ocular, though suited to medium and high-power work, cannot be used to maximum advantage for low magnifications without alteration of the optical system. If, however, this defect could be rectified, a very great saving of time could be made, owing to the use of film packs, as described below. The manufacturers suggest that the only way of overcoming the difficulty is to fit a small lateral ground-glass screen in a funnel-shaped tube with focusing magnifier. The plane of this screen would be at right angles to that of the camera ground-glass screen, but the length of the optical axis would be identical. By focusing on the image the lateral ground-glass screen, perfect focus would be obtained with even the lowest power objectives.[1]

By the use of the Leitz camera an image is obtained in a circular field, the diameter of which just covers the shorter dimension of a 4.5 by 6 cm. film. The photographs show a magnification of 5 to 6, and are therefore larger than those obtained by Stevens and Nelson, although the films used are the same size as their plates.

The Illumination

A single Ediswan "Pointolite" 100–250-volt, 100-c. p. lamp is used facing the observer, in a specially constructed stand, with a small condensing lens; the whole arrangement is shown in Figure 2. The lamp throws a shadow of the specimen between it and the observer, but this is not a disadvantage, as it gives a certain realistic stereoscopic effect to the photograph (see Figures 4 and 5).[2]

The Film

The use of film packs, apart from any question of convenience in handling, is an advance in safety and economy of storage. Films take up much less room than plates, and are unbreakable. The Imperial Panchromatic film pack has been found ideal.

The Filter

Originally a green color filter, recommended by the Imperial Dry Plate Company, was used; more recently the Ilford micro 5 orange filter has been found to give even better contrast, with no sacrifice of detail, and allows a considerably shortened exposure. The K3 Wratten filter mentioned by Stevens and Nelson is deep yellow and probably similar in optical properties to the micro 5. Using the developer mentioned below, the correct exposure was found to be as follows:

Filter	Exposure	Development
	Sec.	*Min.*
K3	15	15
Micro 5	2	15

Figure 4. Print from Whole Negative

Showing confines of illuminated area and typewritten animal serial number corresponding with specimen G332.

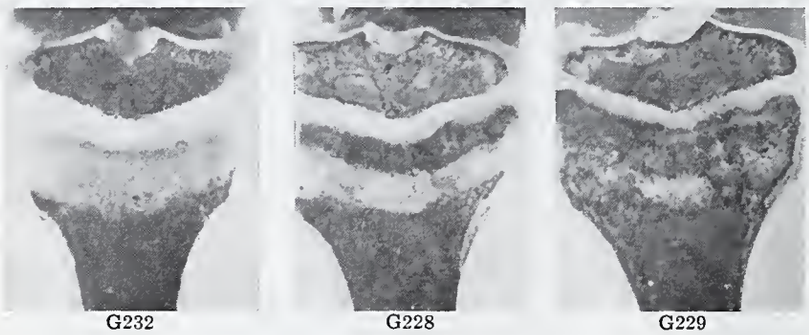
The print reproduced in Figure 4 was made with the short exposure and the orange filter, those in Figure 5 with the longer exposure and green filter.

All exposures have been made with the center of the

[1] Since this paper was written, the authors have received from Messrs. E. Leitz a camera attachment with the ocular redesigned on the suggested lines. It behaves exactly as the manufacturers foretold, with the further advantage that it permits the image to be focused without removal of the orange color filter, thus making a reduction in the number of necessary movements by the operator. A routine worker, using the new attachment and film packs of 12, can photograph 12 lines in 20 to 25 minutes. The camera-attachment is, the authors are informed, obtainable from any of the branch houses of the manufacturers.

[2] Owing to the different relative positions of the axes of camera and ocular in the new apparatus, it has been found more convenient to work with the lamp to the right of the operator, the microscope and camera immediately in front of him, and the ocular pointing towards him. The image of the object so obtained is seen sideways by the observer, instead of upside down, as before.

"Pointolite" bulb about 17 cm. from the specimen. Modern films have very great latitude, and the precise exposures may vary considerably without seriously affecting the quality of the negative, but the same exposure and development should be given to all films, if it is desired also to make prints with a constant exposure. For development, which takes place in a Kodak tank after removal of the backing paper from each film, a 10 per cent Rodinal solution is used for 15 minutes at 19° to 20° C.; the films are fixed in any good acid fixing bath, and washed and dried in the usual way.



G232 G228 G229

FIGURE 5. TRIMMED FINISHED PRINTS

G232, severe rickets
G228, marked healing
G229, advanced healing

Contrary to Stevens and Nelson, the authors have a preference for a white background on the print. Each specimen is therefore placed in a flat-bottomed thin glass dish, which in turn rests on a piece of white paper, and on this is typed the serial number of the animal whose bone is being photographed. This number thus appears photographed on the negative—a feature that, for recording purposes, is of outstanding importance. If a black background is preferred, a strip of white paper with the number typed on can, of course, be used. The typing is placed in such a position relative to the specimen that it can be trimmed off the finished print without trimming off any of the essential part of the bone photograph (see Figures 4 and 5). The specimen is just covered with water, and kept submerged by gently pressing the broken end of the shaft (which does not appear in the photograph) into a small piece of plasticine; this may, if desired, be fixed onto the bottom of the dry dish. If a series of photographs is being taken, it is important to change the water in the dish quite frequently; otherwise, owing to the heat from the lamp, steaming may affect the sharpness of the image.

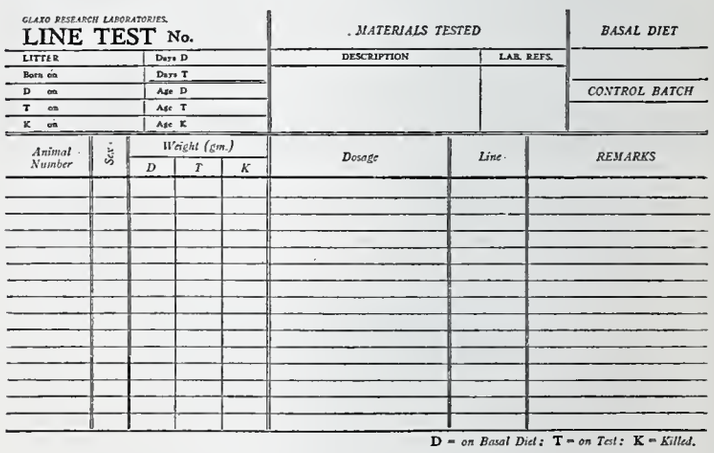
The choice of film packs rather than plates was determined by another consideration. The authors had hoped to focus each specimen solely by means of the ocular. In that case, after each exposure the next film in the pack would simply have been brought into position without removing the film pack adapter from the camera, and the next specimen placed under the microscope and focused; as it is, the film pack adapter has to be removed and each specimen focused afresh on the ground-glass screen. If the trouble with the focusing ocular could be overcome, at least a 50 per cent saving of time could be effected in photographing a series of six or more lines.[1]

Development in total darkness is secured by means of the developing tank, but the usual green safe-light can be discreetly employed while the pack is being unloaded and the films transferred to the tank.

PRINTING

If the negatives are of the right quality, "vigorous" or "contrasty" paper should not be necessary for the prints, which can be made on any good quality medium or normal gaslight[3] paper, developed with amidol and fixed, glazed on glass or on ferrotype, and dried in the ordinary way. Glossy paper, whatever its esthetic disadvantages, is used in deference to the wishes of block-makers, who prefer it; the photographs lend themselves admirably to halftone reproductions (Figure 5. See also Winton and Bayliss, *2*). The finished prints from one test can either be mounted on a card to bring together the results of the test, or stored in a small envelope, as can the negatives, even when as many as twelve refer to a single test. It is convenient to keep a card of mounted prints along with the line-test record card (Figure 6), and also a spare set of prints for each test. Details of the test can be entered on the envelope of films as well as on the record card.

Certain investigators state that they prefer the method of pen-drawing or the use of the camera lucida to actual photographic recording, even, in one case, after a considerable trial of the latter. Their preference is probably based on their experience that uncalcified portions of the bone which have darkened for irrelevant reasons—incomplete removal of blood, over-staining of the whole bone, etc.—are recorded by the camera in the same way as the calcified portions normally stained with silver, whereas the pencil or the camera lucida drawing can record the allowance made by the observer for those defects of staining technic which are never wholly absent. The authors agree with Stevens and Nelson that correct photography should distinguish between the true black-stained calcified tissue and other darkened portions of the bone. In our experience it is only the rare, extreme case in which the photographic record does not allow at least as accurate a diagnosis as that made by direct observation, provided the photograph has been taken with a technic adapted to secure the proper color corrections, by the use of panchromatic films or plates and a suitable filter.



GLAXO RESEARCH LABORATORIES.
LINE TEST No.

LITTER	Days D		
Born on	Days T		
D on	Age D		
T on	Age T		
K on	Age K		

MATERIALS TESTED	
DESCRIPTION	LAB. REFS.

BASAL DIET

CONTROL BATCH

Animal Number	Sex	Weight (gm.) D	T	K	Dosage	Line	REMARKS

D = on Basal Diet; T = on Test; K = Killed.

FIGURE 6. LINE TEST RECORD CARD

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(2) Winton, F. R., and Bayliss, L. E., "Human Physiology," Figure 97, p. 233, Blakiston, 1931.

RECEIVED June 21, 1932.

[3] The term "gaslight paper" is used in Great Britain for slow developing paper, of such speed that a normal negative requires from 5 to 15 seconds' exposure at 12 inches from a 50- to 100-candle-power lamp, and is fully developed in 30 to 60 seconds.

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Shorter Method for Determining Copper Iodometrically

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THE investigations of Haen (*3*), Rümpler (*7*), and Gooch and Heath (*2*) have established the fact that the determination of small amounts of copper (150 mg.) can be accomplished accurately, precisely, and quickly in the presence of ions which interfere in several other methods. However, there is disagreement among these investigators as to the effect of small quantities of mineral acids on this determination. Gooch and Heath say that not more than 3 per cent by volume of hydrochloric, nitric, or sulfuric acid can be present, but Moser (*5*) says that the presence of 5 per cent of sulfuric acid actually improved the determination. This question of the amount of mineral acids allowable is important because in the present method of expelling these acids (*1*) it is necessary to heat to the point of solidification. This procedure is not only time-consuming, but usually causes bumping, with a consequent loss of some material from a beaker even when covered with a watch glass. In addition to this, there is danger of heating too long and producing basic copper salts which are relatively insoluble in acetic acid (*1*).

Moser checked his results electrolytically, whereas Gooch and Heath did not. It was believed that a repetition of their experiments under uniform conditions might point the way to a shorter method, or to a shortening of their methods.

Reagents

Acids. Sulfuric, hydrochloric, nitric, acetic, and tartaric were of c. p. quality, but were each tested by the methods of Murray (*6*) prior to use and found to be satisfactory.

Sodium Thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, was of c. p. quality, tested according to Murray (*6*) and standardized against pure, electrolytic copper.

Copper Nitrate, $Cu(NO_3)_2 \cdot 3H_2O$. These crystals were of c. p. quality, tested according to Murray. The solution used was made by dissolving 5.6 grams in a liter of distilled water at 20° C. The copper content was determined electrolytically by the method given by Hillebrand and Lundell (*4*).

Starch Solution. One gram of Baker's soluble starch was heated to boiling in 100 cc. of distilled water and cooled to 20° C. before use.

Method Used

The general method employed was to take a 50-cc. aliquot portion of the copper nitrate solution, heat till it would just solidify on cooling to room temperature, add the specified amount of mineral acid (see Table I), dilute to 50 cc. total volume with distilled water if necessary, and titrate with standard solution of sodium thiosulfate.

All acids were 8 *N* to compare with the 8 *N* acetic acid used in the standard methods.

Results

The results listed in Table I show that large quantities of mineral acids do cause high results in the iodometric determination of copper, but that 5 cc. of these acids do not cause much higher results than 5 cc. of acetic acid. This suggested that heating all the way to dryness was unnecessary, and a modified method was tried.

The modified method was to add to 50 cc. of copper nitrate solution, 5 cc. of sulfuric acid, 5 cc. of nitric acid, and 5 cc. of hydrochloric acid. Boil gently until the total volume is reduced to about 5 cc. Cool to 25° C., and add 5 cc. of 8 *N* acetic acid, dilute to a total volume of 50 cc. with distilled water, and titrate with standard thiosulfate solution to within about 2 cc. of the end point, add 3 cc. of 1 per cent starch solution, and titrate to disappearance of color.

Table I. Effect of Acids (8 *N*) on Iodometric Determination of Copper

Acid Added	$Na_2S_2O_3$ Soln. Required	Copper Found: Iodometric	Copper Found: Electrolytic	Devn. between Methods
Cc.	*Cc.*	*Gram*	*Gram*	*Gram*
		HYDROCHLORIC ACID		
5	11.40	0.06224	0.06158	+0.00066
10	11.53	0.06265	0.06158	+0.00107
25	11.73	0.06402	0.06158	+0.00242
50	13.15	0.07175	0.06158	+0.01017
		NITRIC ACID		
5	11.32	0.06181	0.06158	+0.00023
10	11.40	0.06224	0.06158	+0.00066
25	11.65	0.06361	0.06158	+0.00203
50	?[a]	.....	.....	.....
		SULFURIC ACID		
5	11.32	0.06181	0.06158	+0.00023
10	11 38	0.06210	0.06158	+0.00052
25	11.54	0.06301	0.06158	+0.00143
50	?[a]	.....	.....	.....
		ACETIC ACID		
5	11.31	0.06176	0.06158	+0.00018
10	11.31	0.06176	0.06158	+0.00018
25	11.30	0.06170	0.06158	+0.00012
50	11.30	0 06170	0.06158	+0.00012
		TARTARIC ACID		
5	11.30	0.06170	0.06158	+0.00012
10	11.30	0.06170	0.06158	+0.00012
25	11.30	0.06170	0.06158	+0.00012
50	11.30	0.06170	0.06158	+0.00012

[a] End point was so variable that no reliable reading could be obtained, but results would have been very high.

This method approximates a method which would be used in getting copper samples into solution, and so has general application. If other proportions of acids were used, the final solution would be similar to this one, because of the higher boiling point of the sulfuric acid present.

Table II. Comparison of Modified Method wth Standard and with Electrolytic Method

Cu Found by Modified Method	Cu Found by Standard Method	Cu Found by Electrolytic Method
Gram	*Gram*	*Gram*
0.06181	0.06170	0.06158
0.06170	0.06181	0.06158
0.06181	0.06170	0.06158
Av. 0.06177	0.06174	0.06158

The per cent difference between the modified and the standard methods is therefore $0.00003 \times 100/0.06174 = 0.048$ per cent ($^1/_2$ part per 1000).

From the foregoing it will be seen that no loss in either precision or accuracy occurs if evaporation of the mineral acids in the standard iodometric method of determining copper is not carried entirely to dryness, provided this evaporation is carried out in the presence of a small quantity of sulfuric acid. This saves time and also does away with the danger of forming insoluble basic copper salts.

The authors think that Gooch and Heath were too conservative in their limit of mineral acids allowable for ordinary analytical work. On the other hand, no evidence was found for the statement of Moser that 5 per cent of sulfuric acid improves the determination, and in this they agree with the findings of Gooch and Heath.

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It is significant that tartaric acid gives more precise results than acetic acid, and the senior author intends to follow this investigation in the hope of explaining the interference of certain acids in this determination.

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Determination of Cadmium

A Critical Study of the Evrard Method

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ALTHOUGH cadmium is a fairly common constituent of many zinc ores and concentrates, there does not exist a rapid and specific method for its determination. In a recent communication Evrard (*3*) reported a method which appeared to be simple and accurate and which functioned in the presence of large amounts of zinc. Inasmuch as such a method is sorely needed, the writers thought it worth while to repeat the work of Evrard and investigate the possibilities of the method.

Evrard's determinations indicated that the cadmium iodide addition product of allyl iodourotropine was quantitatively insoluble and could be represented by the formula $CdI_2[(CH_2)_6N_4.C_3H_5I]_2$. Inasmuch as the molecule contains but 11.44 per cent of cadmium and in light of its reputed insolubility in the presence of excess precipitant or in 95 per cent alcohol, the determination appeared to offer excellent possibilities. Zinc, according to the original author, had little effect upon the determination, for in the presence of large amounts of a zinc salt and in moderate concentrations of sulfuric acid a recovery of 99.7 per cent of added cadmium was obtained.

Experimental Procedure

Preparation of Materials. Allyl iodide, prepared according to the method of Datta (*1*), was added to an equimolar solution of urotropine in chloroform. The melting point of the precipitated allyl iodourotropine checked with accepted values. A 10 per cent aqueous solution was used throughout the work.

Cadmium sulfate was purified by subjecting c. p. material to the treatment described by Reilly (*4*). The recrystallized product, freed from iron and zinc, was dehydrated *in vacuo*, ignited in quartz, cooled, moistened with sulfuric acid, and again ignited. The anhydrous salt was dissolved in water to give solutions containing approximately 0.001 gram of cadmium per cubic centimeter.

Results of Analysis. Evrard reported little detailed information regarding the exact procedure followed in the analysis of his solutions. As nearly as the writers were able to determine, the precipitations were carried out by adding the cadmium solutions to the reagent. This order was followed in a large number of cases, but it was found that the characteristics of the determination were such that the order of addition was relatively unimportant.

The precipitated complex was found to be a white flocculent compound which, in the absence of excess precipitant or other electrolyte, exhibited a marked tendency to pass into the colloidal state. In a series of preliminary analyses an attempt was made to simulate as nearly as possible the conditions recommended by Evrard. The precipitations were made in the cold, and all washings were made in the prescribed manner with a dilute solution of the reagent followed by small portions of 95 per cent ethyl alcohol. An average recovery of 96.4 per cent of the added cadmium was obtained. Although a ninefold excess of precipitant was used in all of the preliminary experiments, it was thought that a further increase might result in a more nearly quantitative recovery. Accordingly a study was made of the effect of excess reagent. It was found that, when an amount of allyl iodourotropine representing a fourteen fold excess was employed, the apparent recovery reached 116.1 per cent. Decreasing the amount of reagent resulted in decreased recoveries.

From a study of the data obtained during the execution of some hundred analyses, it became apparent that erratic recoveries of added cadmium resulted from two principal causes. Incomplete removal of reagent or salt adsorbed by the precipitate gave rise to a positive error, whereas the actual solubility of the precipitate contributed to significant negative errors. In such cases it is only by a fortuitous balance of conditions that results approaching theoretical are obtained.

Inasmuch as the precipitate is somewhat less soluble in alcohol than in water, it appeared worth while to attempt to carry out the determination in alcoholic solution. Accordingly numerous analyses were made on solutions, the ethyl alcohol content of which varied from 45 to 67 per cent by volume. Cadmium recoveries ranging from 32.5 to 129.4 per cent were obtained. Prolonged washing with ethyl alcohol dissolved a major portion of the precipitate.

Although solutions of zinc salts do not yield precipitates when added to allyl iodourotropine solutions, the presence of zinc has a marked effect upon the cadmium determination. Apparent recoveries of as high as 132 per cent of added cadmium were obtained when the determination was carried out in the presence of small amounts of zinc. The obvious inference is that zinc is co-precipitated or otherwise carried out of solution when the cadmium complex is precipitated. Sulfuric acid in concentrations of 0.01 to 0.05 *M* had little effect on the solubility of the precipitate. Only when the concentration exceeded 0.06 *M*, was the relative percentage of cadmium recovered greatly decreased.

A series of solubility determinations carried out at 25° ± 0.5° C. indicated that the complex was soluble to the extent of 0.0014 gram per cc. of water. The solubility in ethyl alcohol was somewhat less, an average of 0.00062 gram per cc. being obtained.

The use of allyl iodourotropine as a qualitative reagent was also investigated. It was found that a number of metallic ions formed insoluble complex derivatives when treated with the reagent. This is in harmony with the results of

Delépine (*2*), who found that the base was precipitated by $HgCl_2$, $HgBr_2$, HgI_2, $KBiI_4$, and other salts. Following are the approximate molar concentrations at which precipitation of various metallic derivatives of allyl iodourotropine take place.

Salt	Molar Concn.	Salt	Molar Concn.
$SbCl_3$	5×10^{-4}	$Hg(NO_3)_2$	4×10^{-4}
$Bi(NO_3)_3$	5×10^{-3}	$SnCl_2$	6.7×10^{-3}
$FeCl_3$	7×10^{-3}	$CuCl_2$	5×10^{-3}
$PbCl_2$	2.4×10^{-7}	$AsCl_3$	1×10^{-3}

Pentavalent arsenic and antimony do not yield precipitates when treated with the reagent. Likewise molar solutions (or in some cases saturated) of LiCl, NaCl, KCl, $BaCl_2$, $CaCl_2$, $SrCl_2$, $Mg(NO_3)_2$, $ZnSO_4$, $Al(NO_3)_3$, $La(NO_3)_3$, $Ce(NO_3)_3$, $Ce(NO_3)_4$, $ZrOCl_2$, $Th(NO_3)_4$, $SnCl_4$, $MnCl_2$, $KReO_4$, $CrCl_3$, $NiCl_2$, and $FeSO_4$ do not form insoluble complex allyl iodourotropine derivatives.

The use of allyl iodourotropine as a precipitant for cadmium is, therefore, not a reliable method because of solubility and adsorption errors. The interference of other metals has been indicated.

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Determination of Fluorine in Cryolite

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The determination of fluorine in minerals containing appreciable amounts of this element has always been accomplished by difficult and tedious procedures which, at their best, have left much to be desired. Many compounds have been proposed for the gravimetric determination of fluorine, the most common of which are: calcium fluoride (*3*), lanthanum fluoride (*10*), thorium fluoride (*12*), and lead chlorofluoride (*15*). While good results have been reported in some cases, preliminary trials proved none of these methods applicable to complex compounds of high fluorine content such as cryolite, except that in which the fluorine was precipitated as lead chlorofluoride.

The volumetric methods of Hempel and Scheffler (*5*), Wagner and Ross (*16*), and Penfield (*11*), which depend upon the evolution of the fluorine as silicon tetrafluoride, are impractical, as it is not possible to recover all the fluorine by such distillations. According to Reynolds, Ross, and Jacob (*13*), 92 per cent is about all that can be obtained by the best available procedures. Shuey (*14*) has made an investigation of the recovery of fluorine from sodium fluoride and states that the average of the results obtained would suggest the possible use of a factor in placing the recovery of fluorine on a 100 per cent basis. His results, for the most part, are rather inconsistent and it is felt that the use of a factor would be unreliable.

Kurtenacker and Jurenka (*8*) have proposed the use of cerous nitrate as a reagent for the direct titration of fluorine using methyl red as an indicator. More recently Batchelder and Meloche (*1*) have outlined a procedure involving the use of ampho magenta as an adsorption indicator for the direct titration of fluorine by means of cerous nitrate. Data have been given showing a comparison of results obtained by this method and those obtained by the method of Kurtenacker and Jurenka. According to Batchelder and Meloche, methyl red gave slightly better results in the case of smaller quantities of fluoride, and in a later publication (*2*) they have given further details concerning this reagent. It has been the writer's experience that methyl red is the more satisfactory of the two indicators. Kurtenacker and Jurenka reported difficulty in obtaining results in agreement with the theoretical values based upon the cerium content of the solution added. Differences amounting to about 4 per cent have been observed by them. This has been the writer's experience in nearly all cases. Batchelder and Meloche reported no such discrepancy.

Determination of Fluorine Using Yttrium Nitrate

The writer has found that yttrium nitrate may be used as a satisfactory reagent for the direct titration of fluorine using methyl red as an indicator. Quantities of sodium fluoride ranging from a few tenths of a milligram to 0.3 gram were titrated with equally good success. In pure solutions the results were in close agreement with the theoretical values based upon the yttrium content of the solution added. However, titrations could not be made at 80° C. as in the case of cerous nitrate.

It was found that potassium chloride and nitrate produced errors varying from −3.3 per cent at 1 gram per 100 ml. to −6.2 per cent at 4 grams per 100 ml. with practically no increase up to 8 grams per 100 ml. The corresponding sodium salts produced an error varying from −1.2 per cent to −3.8 per cent under the same conditions. Mixtures of potassium and sodium salts gave errors varying from −2.3 per cent at 0.5 gram per 100 ml. to −6.2 per cent at 4 grams per 100 ml. Sulfates caused an over-titration in concentrations greater than 0.1 gram per 100 ml.

Materials Used. The sodium fluoride used as a primary standard was furnished through the courtesy of V. W. Meloche, of the University of Wisconsin. Several sodium determinations, as well as tests for impurities, showed the material to be of excellent quality. Natural cryolite obtained from Greenland was used for these experiments. The material was very carefully selected by hand and gave the following analysis:

	Theoretical	Found
	%	%
Na	32.86	32.85
Al_2O_3	24.26	24.25

White reagent-grade cerous nitrate was used. The solution was standardized according to the method of Metzger (*9*) and showed a purity of 99.0 per cent as compared to the cerium determined gravimetrically. Reagent-grade yttrium nitrate was used, which tests showed to be of a good quality. This reagent may be readily obtained in pure form.

Proposed Method

After a thorough investigation of the methods already described, it was decided that the use of yttrium nitrate for the direct titration of fluorine in cryolite offered the best possibility.

Standard Solution of Yttrium Nitrate. Dissolve approximately 16 grams of $Yt(NO_3)_3 \cdot 4H_2O$ in one liter of water. Heat the solution to boiling and continue to boil for 2 to 3 minutes. After allowing to stand overnight the solution is filtered and standardized against a neutral solution of pure sodium fluoride containing approximately the same amount of sodium and potassium nitrates as will be present in the unknown. The titration is made at room temperature using methyl red as indicator. The volume of the solution and the amount of fluorine in the blank should be approximately the same as that in the unknown.

Fusion of Sample. Mix intimately in a platinum crucible, by means of a platinum wire, 0.5 gram of the sample with a mixture of 6 grams of sodium and potassium carbonates and 0.5 to 0.6 gram of finely ground quartz. Cover the crucible with a platinum lid and fuse at a moderate heat for 1 to 1.5 hours. Transfer the crucible containing the cooled melt to a 400-ml. beaker, cover with water, and digest on the hot plate until disintegrated. Filter and wash thoroughly with hot water.

Neutralization of the Solution. Add a few drops of phenolphthalein and add dilute nitric acid (1 to 9) dropwise and with rapid stirring until the pink color is destroyed. Heat the solution to boiling and continue the successive small additions of nitric acid until the sodium carbonate has been reduced to about 0.5 per cent. The volume of the solution should be reduced to about 200 to 250 ml. Now add, dropwise and with rapid stirring, a neutral solution of zinc nitrate (10 per cent) until the pink color of the indicator no longer reappears. Continue the boiling for 2 to 3 minutes. Filter and wash thoroughly with hot water. Add dilute sodium hydroxide (0.25 *N* carbonate free) from a buret until the solution is just a faint pink. Evaporate the solution to a volume of about 150 ml. and transfer to a 200-ml. volumetric flask. Cool to room temperature, make up to mark, mix well, and filter into a dry flask.

Titration of the Solution. Transfer 100 ml. of the solution to a 250-ml. beaker and make exactly neutral to phenolphthalein. Add 3 to 4 drops of methyl red and titrate at room temperature with a standard solution of yttrium nitrate.

The error produced by alkali salts may be easily corrected by adding to the blank determination the approximate amount of each corresponding salt which will be present in the unknown or by adding to both sufficient potassium nitrate to give this salt a concentration of 4 to 5 grams per 100 ml.

In concentrated fluoride solutions the sensitivity of methyl red to yttrium nitrate was far superior to that of cerous nitrate, 1 to 2 drops of a 0.04 *N* solution being sufficient to cause a very sharp color change. If, on the other hand, the fluoride concentration was less than 0.025 gram per 100 ml. the sensitivity of the indicator to cerous nitrate was greatly improved, while in the case of yttrium nitrate it was diminished to such an extent as to make its use impractical.

Fusion of Sample. Cryolite may be satisfactorily decomposed by fusing at a moderate heat with a mixture of sodium and potassium carbonates. Silica must be added to aid in the decomposition. The melt disintegrates easily and offers no difficulty in dissolving. For materials containing appreciable amounts of fluorine, Hillebrand (*6*) recommends that the insoluble residue be ignited and the fusion and extraction repeated. In this work only occasionally was as much as 1 mg. of fluorine found in the residues. Hawley (*4*) recommends that the insoluble residue be boiled with a strong solution of sodium carbonate to extract the last trace of fluorine. This is only a precautionary measure and is of no value unless the original fusion was properly carried out.

Neutralization of Solution. It was found that neutralization could be effected completely and in a relatively short time by adding dilute nitric acid at boiling temperature, using phenolphthalein as an indicator until the sodium carbonate in the solution was reduced to about 0.5 per cent, and finally completing the neutralization by the addition of a small excess of a neutral solution of zinc nitrate. After the solution was filtered, the excess zinc was removed by the addition of dilute sodium hydroxide until the phenolphthalein just turned pink.

After transferring the solution to a volumetric flask, filtered portions were titrated with standard solutions of yttrium nitrate and cerous nitrate. Another portion of the solution was used for precipitating the fluorine as lead chlorofluoride, which was dissolved and the chlorine titrated according to the method of Hoffman and Lundell (*7*).

Fluorine in a Bureau of Standards sample of opal glass, No. 91, was also determined in a further effort to test the adaptability of the method to glasses and enamels. Yttrium nitrate gave unsatisfactory results and could not be used. The results are given in Table I.

Table I. Comparison of $Yt(NO_3)_3$, $Ce(NO_3)_3$, and PbClF Methods for Determination of Fluorine

(Results calculated on basis of 0.25-gram sample for $Yt(NO_3)_3$ and $Ce(NO_3)_3$, and 0.1875-gram sample for PbClF)

Material	Fluorine Present	Fluorine Found[a] $Yt(NO_3)_3$[b]	$Ce(NO_3)_3$[c]	PbClF
	%	%	%	%
Cryolite	54.29	54.29	54.15	53.43
Cryolite	54.29	54.24	54.08	53.33
Cryolite	54.29	54.24	54.05	53.27
Cryolite	54.29	54.22	53.93	53.27
Cryolite	54.29	54.19	53.91	53.23
Cryolite	54.29	54.13[d]	54.10[d]	...
Cryolite	54.29	54.13[d]	54.05[d]	...
Opal glass	5.75[e]	...	5.76	...
Opal glass	5.75	...	5.74	...
Opal glass	5.75	...	5.71	...
Opal glass	5.75	...	5.71	...
Opal glass	5.75	...	5.70	...

[a] No determinations made where blanks are shown.
[b] Titration made at room temperature.
[c] Titration made at 80° C.
[d] Residue boiled with 50 ml. of 2 per cent sodium carbonate.
[e] Certificate value of Bureau of Standards opal glass No. 91.

Summary

A volumetric method has been outlined for the determination of fluorine in cryolite, using yttrium nitrate as a reagent. The method did not succeed when the amount of fluorine was less than 0.025 gram per 100 ml. The effects of alkali salts are shown. Neutral solutions must be used in all cases.

The lead chlorofluoride method gave low results. Cerous nitrate is recommended as a reagent for the determination of fluorine in glasses. A rapid method has been outlined for the neutralization of the solution.

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Correction. As a result of a study of methods of solution of cubic equations, which fit the curves for certain potentiometric titrations in the region of the end point, I deduced the formula for finding the inflection published in Ind. Eng. Chem., Anal. Ed., **4**, 144 (1932). Not until after publication of that paper was it brought to my attention that in *Z. anal. Chem.*, **69**, 417 (1926), Hahn employs what is essentially the same method. I regret that I did not know of his solution earlier; recognition of it would have saved me considerable work.

Florence Fenwick

A Colorimetric Method for the Determination of Tartaric Acid

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In attempting to develop a colorimetric method for the determination of tartaric acid or tartrates, various color reactions of tartaric acid were investigated. The only one which showed promise of being applicable is that first described by Fenton (*2*, *3*). In this test a violet color is produced when a tartrate is treated with ferrous sulfate, hydrogen peroxide, and sodium hydroxide. This color reaction appears to be specific for tartaric acid. Fenton found that citric, succinic, malic, and oxalic acids and sugar do not give the test, and these observations have been confirmed by the authors.

In the following report a method is described whereby Fenton's color reaction for tartaric acid is made the basis of a quantitative colorimetric method for its determination. It has been found to give good results on solutions of pure tartaric acid, on tartrate baking powders, and on tartrate baking powders in the presence of aluminum.

Preparation of Reagents

One Per Cent Ferrous Sulfate. Dissolve 1 gram of ferrous sulfate in 80 cc. of water, heating gently and stirring to aid solution. Cool, transfer to a 100-cc. volumetric flask, and make up to volume.

Hydrogen Peroxide. Use a good grade of commercial 3 per cent hydrogen peroxide.

Normal Sodium Hydroxide. Prepare an exactly normal solution of sodium hydroxide.

Tartaric Acid Standard Solution. Transfer 16 grams of dry *d*-tartaric acid to a 100-cc. volumetric flask, dissolve in water, and make up to volume.

Working Tartaric Acid Standard Solution. Transfer 5 cc. of the tartaric acid standard solution to a 100-cc. volumetric flask, add 10.66 cc. of normal sodium hydroxide solution and make up to volume. This solution contains 0.80 gram of tartaric acid per 100 cc. and has a pH of 6.2.

Analytical Procedure for the Analysis of a Tartrate Baking Powder

Transfer to a small beaker a 2-gram sample of baking powder. Add water, drop by drop, until carbon dioxide ceases to be evolved. Next add 45 cc. of water and stir thoroughly to dissolve the tartrates present. To remove the starch, filter into a 100-cc. volumetric flask and wash the residue three times with 15 cc. of water at each washing. Make up to volume with water. This solution should have a pH of approximately 6.2. If the pH varies from 6.2 by more than ± 0.5, another sample should be prepared and the pH adjusted before making up to volume. The pH of the solution may be determined colorimetrically, using chlorophenol red as an indicator. As a rule tartrate baking powders require no adjustment.

Transfer 10 cc. of the above solution to a 25-cc. volumetric flask. Add 0.2 cc. of 1 per cent ferrous sulfate solution and 0.2 cc. of hydrogen peroxide and mix thoroughly. Upon the addition of hydrogen peroxide the solution will turn yellow. Allow the solution to stand until it becomes brownish in color and then place it in an ice bath until the brown color disappears and the color becomes definitely lavender. Add immediately 5 cc. of normal sodium hydroxide solution. Stopper the flask, mix by inversion twice, and place the flask in the ice bath for ten minutes. At the end of this time remove the flask from the ice bath, mix by inversion twice, and compare in a colorimeter with a standard prepared simultaneously. For the standard, 10 cc. of the working tartaric acid standard solution containing 0.08 gram of tartaric acid are used. The results may be calculated from the following formula:

$$\frac{\text{Reading of standard} \times 0.08 \times 10 \times 100}{\text{Reading of unknown} \times \text{wt. of sample}} = \%\ \text{tartaric acid}$$

In Table I are given the analyses of two samples of tartrate baking powder for total tartaric acid by the colorimetric method and by the official method (*1*) of the Association of Official Agricultural Chemists. It will be noted that the colorimetric method in both cases gives slightly higher results than the A. O. A. C. method. The lower results in the A. O. A. C. method may be due to incomplete precipitation of potassium acid tartrate or its slight solubility in the alcohol which is used in washing the precipitate.

Table I. Analyses of Tartrate Baking Powders for Total Tartaric Acid

	Colorimetric Method		A. O. A. C. Method
	%		%
		Sample 1	
	39.8		39.6
	40.0		39.4
	39.6		39.6
	39.6		39.7
	39.8		39.5
Av.	39.76		39.56
		Sample 2	
	34.8		34.3
	34.6		34.2
	34.5		34.2
	34.8		34.3
	34.6		34.2
Av.	34.66		34.24

In order to check further the reliability of the colorimetric method, samples of baking powder were prepared containing known amounts of tartaric acid. In Table II results of analyses of these samples by the colorimetric method are given.

Table II. Analyses of Baking Powders by the Colorimetric Method

	Tartaric Acid Present				
	%	%	%	%	%
	10.00	15.00	20.00	30.00	40.00
	Tartaric Acid Found				
	9.95	14.92	20.00	30.00	39.80
	10.00	14.92	19.90	30.15	40.00
	9.95	15.00	20.00	29.85	40.00
	10.00	15.00	20.20	30.00	40.21
Av.	9.98	14.96	20.03	30.00	40.00

It was suggested to the authors that the colorimetric method would be especially valuable in the analysis of baking powders if it gave accurate results in the presence of aluminum. To test the method in the presence of aluminum, 5 grams of $AlK(SO_4)_2.12H_2O$ were mixed with 95 grams of baking powder whose tartaric acid content was known. By calculation the mixture contained 38.24 per cent of tartaric acid. The results of five analyses by the colorimetric method gave values ranging from 38.09 to 38.46 per cent, with an average value of 38.31 per cent. It is evident that

the presence of aluminum does not interfere with the colorimetric determination of tartaric acid in a tartrate baking powder.

As a matter of interest the application of the colorimetric method to the determination of other forms of tartaric acid was studied. Using *d*-tartaric acid as a standard, it was found that *l*-tartaric acid, *l*-ammonium tartrate, and *meso*-tartaric acid produce a color equivalent to that of the standard. With racemic acid the color intensity was approximately one-half that of the standard.

This reaction of racemic acid was surprising. It was thought that possibly there might be some union of the *d*- and *l*-forms in racemic acid which was causing an interference in the reaction, but molecular weight determinations by the freezing-point method indicates no such union. With regard to the purity of the racemic acid used (obtained from the Eastman Kodak Company) it may be said that it was optically inactive and that it required the theoretical amount of sodium hydroxide for neutralization. The melting point was 202° C., whereas the accepted value is 205–206° C. A mechanical mixture of equal parts of *d*- and *l*-tartaric acids did not react like racemic acid but gave the proper color intensity. Two different samples of racemic acid were analyzed with identical results. No satisfactory explanation can be made for this behavior of racemic acid. Racemic acid crystallizes with one molecule of water of crystallization, while *d*- and *l*-tartaric acids crystallize in the anhydrous form. This might suggest some difference between the chemical properties of racemic acid and the *d*- and *l*-forms of tartaric acid. *Meso*-tartaric acid also crystallizes with one molecule of water, but it gives the same color as the *d*- and *l*-forms. Hence it appears that the water of crystallization is not a factor in color production.

With regard to the use of this method, the authors feel that certain points should be emphasized. The pH of the standard and of the unknown should be approximately the same at about 6.2. The sample taken should be of such a size that the color of the standard and of the unknown is approximately the same. The amount of ferrous sulfate used should be exactly 0.2 cc. The sodium hydroxide solution should be added as soon as the lavender color appears. The method is not applicable in the presence of calcium or phosphates.

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Determination of Organic Sulfur in Gas

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No method for the determination of organic sulfur compounds in gas has so far been described which combines the speed and convenience of the method by which it is customary to determine sulfur in motor fuels (*1*). The apparatus required for this determination is simple, conveniently handled and transported, and a determination requires about 2.5 hours. In contrast, the well-known Referee method for determining organic sulfur in gas requires from 5 to 10 hours for a determination, and the apparatus required is cumbersome to operate and unwieldy to transport. A review (*2*, *5*, *6*) of the methods in general use for determining organic sulfur in gas will show that all have these difficulties in common. Huff's platinum spiral method (*4*) is very convenient when used on gas containing a large amount of hydrogen and rather small quantities of hydrocarbons. However, when the hydrocarbon concentration is high enough to give appreciable quantities of unsaturated compounds on passing over the platinum spiral, the sulfur found will be too great. This method cannot be used at all on pure hydrocarbon gas, such as refinery gas.

With the exception of the platinum spiral method, all procedures are similar in that a measured volume of gas is burned with air or oxygen. Subsequently, the sulfur dioxide formed by the combustion of the sulfur compounds is removed from the products of combustion in a suitable absorber, and is most frequently determined by precipitation as barium sulfate. The barium sulfate determination requires by far the greatest portion of the operator's attention, and while its accuracy is great, the time spent on this step of the determination may not be justified in view of the errors which may enter at other points. Although volumetric procedures have been proposed (*3*), they are seldom used. Lieber and Rosen have developed a new modification of this general method (*5*), and the accuracy of the procedure as a whole was tested by burning a gas, initially sulfur-free, into which a known amount of pure sulfur compound has been introduced. The average error of seven tests, in which several different sulfur compounds were burned, was slightly more than 1 grain per 100 cu. ft. of gas. The Bureau of Standards states (*2*) that with the Referee method "..... the uncertainty of the experiment may be as great as 1 grain [per 100 cu. ft. of gas] on the average of two tests."

This investigation was undertaken to ascertain whether or not the A. S. T. M. procedure for the determination of sulfur in motor fuels could be modified to give a rapid and convenient method for the determination of organic sulfur in gas. It was believed that no accuracy need be sacrificed, while the time required for a determination would be substantially decreased. Further, if additional time were available for the determination, it would be used in burning additional gas and would result in increased accuracy. The accuracy of the procedure as a whole has been checked by burning a gas of known sulfur content.

Description of Method

The apparatus used is substantially that recommended in A. S. T. M. Designation D 90–30T (*1*) for the determination of sulfur in motor fuels. The liquid fuel lamp is replaced, however, by a gas burner, preceded by a regulator and meter. A schematic diagram of the apparatus assembly is shown in Figure 1. In order that the method may be applicable to gas of any density and calorific value, the burner is constructed with a mixing chamber in which primary air from a compressed air line is mixed with the incoming gas. The supply of air is regulated by a needle valve so that a steady Bunsen flame is obtained, with well-defined blue inner cone. Secondary air for the flame is supplied by gentle suction on the absorber, as in the method used on gasoline.

The products of combustion are drawn through standard sodium carbonate solution contained in the absorption tube recommended by the A. S. T. M. The sulfur dioxide formed by the combustion of the sulfur compounds in the gas is

absorbed by the carbonate solution, and is oxidized to sulfate by the excess air, according to the equations

$$SO_2 + Na_2CO_3 \longrightarrow Na_2SO_3 + CO_2$$
$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

At the end of a determination, the excess sodium carbonate is titrated with standard hydrochloric acid solution using methyl orange as an indicator. The specifications of A. S. T. M. D 90–30T with respect to titration of the solution are followed. The standard solutions used have the following concentrations:

1. Na_2CO_3: a solution containing 3.306 grams of the anhydrous salt per liter. One cubic centimeter of this solution is equivalent to 0.001 gram of sulfur.
2. HCl: a solution containing 2.275 grams of hydrochloric acid per liter. Ten cubic centimeters of this solution neutralize exactly 10 cc. of the sodium carbonate solution.

Using solutions of this strength, the sulfur content of the gas burned is equal to (cc. Na_2CO_3 taken − cc. HCl used) $\times 10^{-3}$ grams. The concentration of sulfur in the gas in grains per 100 cu. ft. is given by the expression:

$$\text{Sulfur concentration} = 1.543 \left(\frac{\text{cc. } Na_2CO_3 \text{ taken} - \text{cc. HCl used}}{\text{cu. ft. of gas burned}}\right)$$

The quantity of sodium carbonate solution introduced into the absorber at the beginning of an experiment is dictated by the estimated concentration of sulfur in the gas to be burned. If the concentration is no greater than 75 grains per 100 cu. ft., and 0.2 cu. ft. of gas is to be burned, 10 cc. of the sodium carbonate solution are sufficient. The volume of solution in the absorber is always made up to 20 cc. with distilled water.

Since the determination of sulfur by this method depends on an acidimetric titration, the gas to be burned must be ammonia-free. If ammonia were present, an indeterminate quantity of acidic oxides of nitrogen would be formed, which would react with the sodium carbonate in the absorber and give a high result for sulfur.

Determination of Accuracy

The accuracy of the method was checked in a manner similar to that used by Lieber and Rosen (*5*). A sulfur-free hydrocarbon gas was burned at a rate of 0.1 cu. ft. per hour. This gas had a calorific value of about 2400 B. t. u. per cu. ft., so that about 240 B. t. u. per hour were dissipated in the absorber. If the gas is burned at a greater rate, the glass chimney and absorber become unduly hot. The rate of flow of the gas was measured by a calibrated capillary flowmeter. A known amount of a pure sulfur compound was introduced into the gas stream and burned in the apparatus. The quantity of sulfur determined by titration of the absorption solution was compared to the amount introduced.

The pure sulfur compounds selected to check the determinations were obtained from the Eastman Kodak Company, with the exception of carbon disulfide which was Baker analyzed c. p. grade, and were used without further purification. The sulfur compounds were dissolved in acetone or benzene to give solutions of the concentrations shown in Table I. The dilutions were made by weighing the sulfur compound into a weighed quantity of solvent. Blank tests on the solvents showed them to be entirely sulfur-free.

Table I. Compounds Used to Check Determinations

Sulfur Compound	Sulfur in Pure Compound	Solvent	Sulfur Compound in Soln.	Sulfur in Soln.
	%		%	%
CS_2	84.2	Benzene	0.81	0.682
$C_5H_{11}SH$	30.8	Acetone	1.67	0.515
$(C_2H_5)_2S_2$	52.4	Acetone	0.696	0.365
			0.139	0.073
$(C_2H_5)_2S$	35.6	Benzene	1.23	0.437
C_4H_4S	38.1	Benzene	1.78	0.678

To carry out a determination of the accuracy of the method about 2 cc. of one of the solutions were introduced into a clean bubbler tube, shown in Figure 1*a*. The exact quantity of the solution was determined by weighing the bulb before and after filling, and from this weight the weight of sulfur introduced into the gas was calculated. The bubbler was then inserted in the gas train in the position *x–x*, Figure 1. The stopcocks were opened, the gas turned on at a rate of 0.1 cu. ft. per hour, and the burner lighted. The chimney of the absorber was immediately placed over the flame, and the products of combustion drawn through the absorption

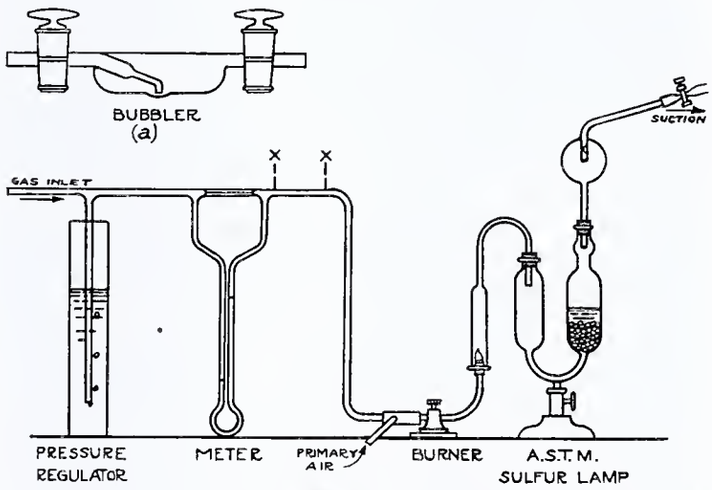

Figure 1. Apparatus Assembly for Sulfur Determination

solution by suction of a water aspirator pump. The test was continued until all the solution had evaporated from the bubbler, and then the gas was burned for about 15 minutes longer to clear the lines of the sulfur compound. From the flowmeter reading and elapsed time, and the calculated volume of the vaporized solution, the total amount of gas burned was obtained. The sulfur content of the gas burned was found by titration of the solution in the absorber, and the concentration of sulfur in the gas in grains per 100 cu. ft. was calculated. The sulfur concentration in the gas varied from about 10 to 75 grains per 100 cu. ft.

Table II. Results of Accuracy Determinations

Sulfur Compound	Gas Burned	Sulfur Sought	Sulfur Found	Sulfur Sought	Sulfur Found	Error	
	Cu. ft.	*Mg.*	*Mg.*	*Grains/100 cu. ft.*		*Mg.*	*Grains/100 cu. ft.*
CS_2	0.318	11.89	11.56	57.7	56.2	0.33	1.5
CS_2	0.213	8.93	8.94	64.6	64.6	0.01	0.0
CS_2	0.318	11.89	11.87	57.7	57.8	0.02	0.1
CS_2	0.256	9.59	9.63	57.8	58.0	0.04	0.2
$C_5H_{11}SH$	0.172	8.12	8.05	72.8	72.2	0.07	0.6
$C_5H_{11}SH$	0.172	8.31	8.36	74.5	75.0	0.05	0.5
C_4H_4S	0.317	11.24	11.24	54.7	54.7	0.0	0.0
C_4H_4S	0.318	11.66	11.82	56.6	57.3	0.16	0.7
$(C_2H_5)_2S$	0.368	7.59	7.53	31.9	31.6	0.06	0.3
$(C_2H_5)_2S$	0.210	4.35	4.30	31.7	31.6	0.05	0.1
$(C_2H_5)_2S_2$	0.172	1.15	1.25	10.3	11.2	0.10	0.9
$(C_2H_5)_2S_2$	0.172	1.15	1.15	10.3	10.3	0.0	0.0
$(C_2H_5)_2S_2$	0.172	1.15	1.10	10.3	9.9	0.05	0.4
$(C_2H_5)_2S_2$	0.172	1.15	1.19	10.3	10.7	0.04	0.4
$(C_2H_5)_2S_2$	0.222	6.02	5.94	41.8	41.2	0.08	0.6
$(C_2H_5)_2S_2$	0.244	8.22	8.36	52.0	52.9	0.14	0.9

The results of the accuracy determinations are given in Table II. The first column gives the type of sulfur compound introduced into the gas for the test. The second shows the total volume of gas burned—that is, the measured volume of hydrocarbon gas plus the calculated volume of vapor obtained from the sample of solution of the sulfur compound. The remainder of the table requires no explanation. The average of column 7 is 0.075 mg., and of column 8 is 0.45 grain per 100 cu. ft. With one exception the error was

never as great as 1 grain per 100 cu. ft. Thus it is apparent that this method is as accurate as any in general use, regardless of whether volumetric or gravimetric methods are used.

Discussion

The data in Table II show that the experimental errors observed are smaller than the maximum error possible due to errors in reading the burets. In the entire procedure, four buret readings are required. If the burets can be read to ±0.02 cc., and if the maximum error is made in all four readings in such a way that they all affect the result in the same direction, the result will be in error by ±0.08 cc. This is equivalent to ±0.08 mg. of sulfur. If 0.1 cu. ft. of gas is burned, this quantity of sulfur is equivalent to ±1.24 grains per 100 cu. ft., but if a greater volume of gas is burned for a determination, the absolute error which may be caused by errors in buret readings is reduced proportionately.

Another source of error in the determination is the methyl orange end point. This error is indeterminable, but it can be minimized by comparing the color of the solution being titrated with the color of a portion of the solution at the end point found on standardization of the solutions. An operator with a little practice, however, usually finds no difficulty in determining the end point to within a drop of hydrochloric acid solution, as the experience of operators using the A. S. T. M. method for motor fuels indicates. This represents an error of about ±0.7 grain of sulfur per 100 cu. ft., when 0.1 cu. ft. of gas is burned in a determination.

Errors in metering the gas burned are common to all methods, and therefore no special mention is required here. These errors have been considered by the Bureau of Standards (*2*).

Thus, from theoretical considerations, as well as from actual determinations, it is believed that this volumetric method is as accurate as any method heretofore used for the determination of organic sulfur in gas.

The speed and convenience of the procedure described in this paper is unsurpassed by any of the methods in general use in the gas industry. A complete determination needs to extend over a period of less than 2.5 hours, and claims hardly 20 minutes of the operator's attention, while a Referee's determination usually requires from two to five times as long.

The A. S. T. M. method for the determination of sulfur in motor fuels has been modified to make it applicable to the determination of organic sulfur in gas.

The accuracy of the method has been checked by burning a gas of known sulfur content, and it has been found to be as great as that of other methods in general use. The average error of sixteen determinations, in which the sulfur concentration in the gas was varied from 10 to 75 grains per 100 cu. ft., was 0.45 grain per 100 cu. ft.

The convenience of this method is greater than that of any other now in use, and the time required for a determination is about one-fourth that required by other methods.

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Rubber Beaker Rings for Accelerating Evaporation on Steam Bath

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The rate of evaporation of a liquid from a beaker placed on top of a steam bath is notoriously slow. If, however, the beaker is supported so that from two-thirds to three-fourths of its length is immersed in the bath (Figure 1), the rate of evaporation can be increased threefold and made fully as rapid as from a porcelain evaporating dish. A convenient support is a rubber ring which fits the beaker snugly enough to hold it in the desired position, and yet slips on and off easily when wetted.

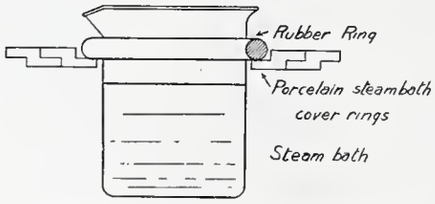

Figure 1. Beaker Supported by Rubber Ring

The size of the ring is determined by the size of the beaker and the difference between the outside diameter of the beaker and the next larger opening in the steam bath. The inside diameter of the ring should be 3 to 5 mm. smaller than the outside diameter of the beaker in order to hold it firmly, and the sectional diameter must be large enough to seat the beaker snugly. The schedule of sizes shown in Table I is suitable for rings to be used with Pyrex beakers of the usual or Berzelius form on a set of porcelain steam-bath cover rings having the specified openings. The rings must be made from rubber compounded to withstand the action of heat and moisture, because ordinary grades of rubber deteriorate in a few days on the steam bath. A satisfactory formula, in parts by weight, is as follows:

Crude rubber	100
Zinc oxide "Kadox" variety	100
Phenyl-β-naphthylamine	1
Stearic acid	2
Tetramethylthiuram disulfide	3
Total	206

Rings of this composition made and vulcanized for 30 minutes at 125° C. showed no swelling, tackiness, or other evidences of deterioration after 500 hours' use on a steam bath.

Table I. Sizes of Suitable Six-Ring Set

Beakers			Rubber Rings	
Capacity	Outside diam.	Steam-Bath Opening	Inside diam.	Outside diam.
Ml.	*Mm.*	*Mm.*	*Mm.*	*Mm.*
150	57	63	54	72
250	68	86	65	96
400	77	86	74	96
600	88	111	85	120
800	99	111	96	120
1000	107	111	104	120

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Assay of Plant Material for Its Rotenone Content

An Extraction Method

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Derris root and cubé root are at present the principal sources of the insecticide rotenone. The chemical evaluation of these roots and of other plant materials containing rotenone is a subject of increasing importance. A method of extraction using carbon tetrachloride has been devised which gives a more selective and ready separation of the rotenone than the ether extraction method previously in use.

THE insecticide rotenone ($C_{23}H_{22}O_6$) is known to occur in a number of fish-poisoning plant materials, such as the roots of various species of *Deguelia* (derris root) found in the Malay Peninsula and the East Indies, the roots of *Lonchocarpus nicou* (locally termed cubé root) of Peru, and the stems of the haiari vine, a species of *Lonchocarpus* native to the Guianas.

In 1923 Tattersfield and Roach (*14*) first proposed a chemical method for evaluating derris root. This consisted, briefly, in exhaustively extracting the finely-powdered, dried root in a Soxhlet apparatus with anhydrous ether, this extract being dried to constant weight at 100° C. The methoxyl content of the extract was then determined because it was known that rotenone contained methoxyl groups and it was felt that this would prove the genuineness of the extract. These investigators found that in three samples of *Deguelia elliptica* the insecticidal value of the root (*7*) bore a direct relationship to the amount of extract.

A method for ether extraction similar to that proposed by Tattersfield and Roach, except that the determination of methoxyl content was omitted, was used by Georgi and Curtler (*8, 9*) in a study of *Deguelia elliptica* and *Deguelia malaccensis*, and has been used by a number of subsequent investigators and by commercial firms. However, it is now known that the ether extracts of both derris and cubé root contain a number of compounds of varying toxicity. It has also been found that several of these—i. e., toxicarol (*1*), deguelin (*2*), and tephrosin (*3*), which have a lower toxicity to insects than rotenone (*6*)—have almost the same methoxyl content as rotenone.

Although the total extracts of derris and cubé roots, which contain a number of materials of insecticidal value, may be widely used commercially, there will be many applications for preparations containing only rotenone. Furthermore, since rotenone is a definite compound of known toxicity to insects (*4, 5, 13*), many manufacturers may wish to standardize their preparations on the basis of the content of this material, rather than on the basis of an extract of unknown composition and toxicity. Consequently, a determination of the amount of rotenone in a root should prove of considerable value.

Ether Extraction Method

A procedure designed primarily for determining the amount of rotenone in the ether extract of these roots has been in use by the Insecticide Division for some time, and was recently outlined by Roark (*12*). Based on the methods adopted by earlier investigators, this method was found to be not entirely satisfactory for all samples of root. For instance, in many cases it was found very difficult to produce crystallization of the rotenone and in some cases no rotenone could be obtained from the ether extract, whereas, as will be shown later, a considerable quantity actually was present. Other ether extracts deposited amorphous material, which interfered with the filtration and gave erroneous results for rotenone.

Accordingly, a search was made for a solvent which would give a more selective separation of rotenone. A material was desired which was a good solvent for rotenone at the temperature of the extraction, but which would not extract too large a proportion of the resinous constituents of the root, and from which the rotenone would separate readily and completely on cooling. Carbon tetrachloride, in which the solubility of rotenone at 20° C. is 0.4 per cent (*11*) and at 65° C. is about 5 per cent, was found to meet these requirements. It is interesting to note that, although Tattersfield and Roach stated that "benzene, dry ether, and carbon tetrachloride . . . . . have a selective dissolving action on the poisons," they found difficulty in drying extracts made with carbon tetrachloride and consequently abandoned the use of this solvent.

Duplicate extractions were made on about twenty samples of derris root, ten samples of cubé root, and two samples of haiari stem (the three sources of rotenone investigated by this laboratory to date), comparing the results obtained by carbon tetrachloride with those obtained by ether. (The results of these and other extractions will be contained in a subsequent article.) As a result of this series of extractions, the following method for the determination of rotenone by carbon tetrachloride extraction was developed.

Carbon Tetrachloride Extraction Method

Fifty grams of plant material ground to about 20 mesh are completely extracted in a large Soxhlet extraction apparatus with carbon tetrachloride. The material should be extracted for 8 to 10 hours (longer for samples giving more than 5 per cent rotenone in this period). It is suggested that the extraction be run overnight (about 17 hours), thus accomplishing a reduction in the actual working time consumed by the method. The extract is concentrated to 50 to 25 cc. in a small beaker flask and set aside for 18 to 24 hours to allow the rotenone to crystallize. The rotenone separates from the concentrated extract as needle-like crystals containing one molecule of solvent of crystallization (*10*). Just before filtering, the extract is cooled for 10 to 15 minutes in ice to assure complete crystallization. The rotenone–carbon tetrachloride solvate is filtered by suction through a tared Gooch crucible containing a disk of hardened filter paper and washed with 10 to 20 cc. of ice-cold carbon tetrachloride in small portions. As much as possible of the excess solvent is removed from the precipitate by suction and then the crystalline material is dried in the crucible to constant weight in air at room temperature (an overnight drying is

sufficient). The solvate is quite stable, and the loss of solvent of crystallization occurs so slowly as to be insignificant in the time mentioned. It is then weighed as the solvate, and this weight multiplied by the factor 0.719 (the ratio of $C_{23}H_{22}O_6$ to $C_{23}H_{22}O_6 \cdot CCl_4$) gives the weight of rotenone.

If the amount of total extract is desired, the filtrate is freed from carbon tetrachloride by evaporation and dried for one hour at 105° C. This weight added to the weight of rotenone gives the total carbon tetrachloride extract (without solvent of crystallization).

Shortened Procedure

Reasonably complete crystallization of rotenone from the evaporated extract may be obtained by cooling the extract, seeding with a small crystal of the solvate compound, and allowing to stand in ice, with occasional stirring, for only 2 to 3 hours. The separated solvate crystals may be freed of excess solvent by drying in an air draft for 3 to 4 hours. By using the overnight extraction, the time required for the whole method is thus reduced to 24 hours or one actual working day. This shortened procedure will give sufficiently good results for many purposes, although the longer method is recommended for more accurate values.

Discussion of the Carbon Tetrachloride Method

Condition of Sample. This method was designed for samples of roots as received without additional drying. Such roots are usually thoroughly air-dried by the time they reach this country. The moisture content of our samples of derris root, as determined by vacuum drying at 100° C., averaged about 3 per cent, while that of cubé root samples was slightly higher, no doubt because of the shorter shipping distance and the larger size of the roots. This content of moisture in no way interferes with the determination of rotenone by the method described above. If, however, the sample contains over 5 per cent moisture, as was the case with one cubé root and one haiari stem sample received, the material should be air-dried at not much over room temperature before extraction.

Oven-drying of samples of derris root before extraction was found to interfere with the results of the carbon tetrachloride extraction. Thus, the value for rotenone obtained from one sample of derris (No. 402)[1] was lowered from 1.4 per cent to 0.9 per cent by drying the root in a vacuum oven at 100° C. for 5 hours. Furthermore, the rotenone obtained by extraction of the dried material was tan in color, while that from corresponding extractions, made without previous drying, was white. Similar results were obtained on this same sample by the ether extraction method. It had been previously noted that samples of root dried at 100° C. for several hours gave much darker ether extracts than those extracted as received.

A fineness of about 20 mesh was chosen as the most adaptable to this method. It was felt that coarser grinding would lead to incomplete extraction, whereas finer grinding appeared unnecessary.

Weight of Sample. In using the original ether extraction method it was necessary in many cases to use 100 grams of sample in order to produce crystallization of the rotenone. However, since the usual large-size Soxhlet apparatus conveniently holds only 50 grams of ground root, it was desirable to use a sample of this smaller size. No difficulty has been experienced in obtaining crystallization from extracts made by the carbon tetrachloride method of 50 grams of samples actually containing over 0.3 per cent rotenone.

Time of Extraction. It was found that an 8-hour extraction is sufficient for samples of low rotenone content. Thus, a sample of derris root (No. 549) giving 1.9 per cent rotenone, and another derris sample (No. 535) giving 4.5 per cent rotenone in 8-hour extractions by this method, gave no more rotenone on additional 7-hour extractions. However, samples giving over 5 to 6 per cent rotenone in an 8-hour period should receive further extraction. For example, a sample of cubé root (No. 686-A) yielding 10.2 per cent rotenone in 8 hours, gave 1.0 per cent more upon an additional 7-hour extraction.

Some carbon tetrachloride extractions were followed by short acetone extractions with the idea that any remaining rotenone would be extracted by this solvent, since acetone is a good solvent not only for rotenone, but also for the resinous material in which the rotenone may be bound. One sample of derris root (No. 522) extracted 10 hours with carbon tetrachloride gave 6.7 per cent rotenone. The marc was extracted for 4 hours with acetone, the extract evaporated to dryness, taken up in hot carbon tetrachloride, filtered to remove insoluble material, and allowed to cool. No further rotenone separated. On the other hand, another sample (No. 594-B) gave about 6 per cent rotenone on a 10-hour carbon tetrachloride extraction, with 0.3 per cent additional impure rotenone on acetone extraction. A third sample of root (No. 956) gave about 6 per cent in 10 hours with carbon tetrachloride and an additional 1 per cent with acetone. A 17-hour (overnight) carbon tetrachloride extraction of this last sample gave the full 7 per cent rotenone, however, showing that the rotenone is completely extracted from such a sample by carbon tetrachloride if sufficient time is allowed. It is for these reasons that an overnight extraction is recommended.

The temperature of the solvent is probably a factor in the rate of extraction. In these experiments the carbon tetrachloride was kept actively boiling throughout the extractions. Under these conditions the temperature of the solvent surrounding the root remained at about 70°.

Crystallization and Filtration of the Rotenone. In all extractions made in this laboratory, the rotenone, when present in quantities larger than 0.3 per cent, has readily crystallized from the evaporated carbon tetrachloride extract on cooling. In a few cases, when less than 1 per cent of rotenone was present, it was necessary to seed the cold extract with a small crystal of the solvate, and when this was done, the crystalline material separated quickly. Usually scratching the inside of the flask with a glass rod was sufficient to induce crystallization and, in most cases, even this was unnecessary. If the extract evaporates to a gummy consistency, crystallization may often be produced by the addition of a small amount of cold carbon tetrachloride. The procedure of cooling the extract in ice for 10 to 15 minutes before filtering was adopted to insure more nearly complete separation of the rotenone. A good plan is to place the concentrated extract in a refrigerator overnight.

The separated rotenone should be washed with as small an amount of cold solvent as possible. Although the solubility of rotenone in carbon tetrachloride at 0° C. is very low, an appreciable loss may occur if the rotenone is washed too extensively. In our experiments the solvate was washed until the filtrate was colorless.

Purity of the Separated Rotenone. An examination of the purity of the separated rotenone is an important point in any quantitative extraction method. Something in the nature of a check result may be obtained by heating the separated solvate compound to drive off the carbon tetrachloride of crystallization and reweighing as pure rotenone. This may be accomplished by heating the separated crystalline material for one hour at 105° C., when the material usually "melts" to a glassy mass (due to the presence

[1] These numbers refer to Insecticide Division samples and are given for convenience in comparing with subsequent extraction results.

of the solvent of crystallization). Check results were obtained in this way on 6 samples of derris and 2 samples of cubé.

A determination of the optical rotation of the separated rotenone is of value as an indication of its purity. This should be made on the material from which the carbon tetrachloride of crystallization has been removed, as the presence of this solvent may cause incorrect values. This determination should be made in benzene because of the high rotation of rotenone in this solvent. If it is assumed that the impurities are optically inactive, the apparent purity of the rotenone may be calculated from the optical rotation (*11*). However, many of the impurities likely to be present may possess optical activity, and hence the result of such a calculation will be only approximate.

In all extractions made in this laboratory a small portion of the separated crystalline material was recrystallized, and microscopic examination and melting point determinations were made. At first, ethyl alcohol was used for this purpose, but it was found that in many instances alcohol gave odd-shaped lathlike crystals with erroneous melting points when the substance was actually known to be quite pure rotenone. This may be due to the formation of an alcohol solvate as suggested by Tattersfield and Roach (*14*), although the author was unable to obtain such a solvate from pure rotenone (*10*). Amyl acetate was finally found to be a most suitable solvent for this purpose. It consistently gave the characteristic hexagonal plates of rotenone. The melting points of the recrystallized materials obtained in this way ranged from 155° to 163° C. The melting point of this material mixed with rotenone of known purity may also be obtained. The three other crystalline substances thus far isolated from either derris or cubé—i. e., toxicarol, deguelin, and tephrosin—if present in the separated crystalline material, would be recognizable by their different crystallographic properties, but their presence has not been detected. According to Clark's work (*1*, *2*, *3*) on these materials, their presence in the separated crystalline material would be unlikely, as they are ordinarily obtained by alkali treatment of the mother liquors from the rotenone separation.

It is possible that a determination of the chlorine content of the crystalline solvate would give some indication of the purity of the rotenone. The determination of the methoxyl content of the separated rotenone should also be of value.

Drying the Noncrystalline Extract. In the extractions made in this laboratory, the carbon tetrachloride was removed from the filtrate after the rotenone separation by heating on the steam bath in a draft of air until no odor of the solvent was detected and then drying the residue at 105° C. for one hour. It was found that a one-half hour drying was not sufficient. These filtrates were dried in shallow aluminum dishes.

The difficulty encountered by Tattersfield and Roach (*14*) in drying carbon tetrachloride extracts was no doubt due to difficulty in removing the carbon tetrachloride of crystallization from the rotenone.

Accuracy of Method. The accuracy of an extraction method of this type depends primarily on the thoroughness of the extraction and the completeness of the crystallization from the extract. The solubility of rotenone in carbon tetrachloride at 20° C. is 0.6 gram per 100 cc. of solution, so that the 25 cc. of extract in this method might hold 150 mg. of rotenone in solution. In a 50-gram sample this would amount to 0.3 per cent of the original root. The resinous materials present might be expected to increase this solubility slightly. On the other hand, the fact that the extract is cooled in ice should markedly decrease error from this source.

In order to determine the approximate accuracy of the carbon tetrachloride extraction method, mixtures were made of different amounts of pure rotenone with a derris root (No. 401) which was known to contain no rotenone. This root had given from 0.2 to 0.3 per cent separated material from ether extractions, but on careful examination this material was found to contain no rotenone. Carbon tetrachloride extractions of the same root gave less than 0.1 per cent separated material, which again was found to contain no rotenone. Mixtures of this root with pure rotenone, containing 0.3, 0.5, 2.0, and 5.0 per cent rotenone, were prepared and extracted by the method in question for 10 hours. No crystalline material could be separated from the 0.3 per cent mixture; the 0.5 per cent mixture gave exactly 0.5 per cent, the 2.0 per cent gave 2.3 per cent in two determinations, and the 5.0 per cent gave 5.2 per cent in two determinations. It would appear from these results that the method is of no value for samples containing 0.3 per cent, or less, rotenone. On the other hand, when sufficient rotenone is present to produce crystallization (over 0.3 per cent), the method gives correct or slightly high results. The latter effect is no doubt due to incomplete washing when large quantities of rotenone are separated. As already noted, however, too much washing is not advisable because of the possibility of loss. It is believed that this method, when properly handled (including examination of the separated crystalline material by the methods outlined to make certain that it is entirely rotenone), and used on samples containing over 0.3 per cent rotenone, will give results which differ from the true values by not more than +0.3 per cent. Probably no extraction method will give more accurate results than this. A chemical method is undoubtedly needed to obtain exact results on the rotenone content.

It is suggested that when no rotenone can be crystallized from an extract by this method, a larger sample should be used, in order to reduce the proportion of solvent to rotenone in the evaporated extract.

Superiority of Method over Ether Extraction. In general, carbon tetrachloride was found to give a much more selective separation of the rotenone than is possible with ether. Four samples of derris root (Nos. 408, 524, 537, and 739), which gave no rotenone by ether extraction, even when the concentrated extract was seeded with a few crystals of rotenone, readily yielded crystalline rotenone when the carbon tetrachloride method was used, the rotenone amounting in each of the four cases to about 2 per cent of the root. About 1 per cent rotenone was obtained by carbon tetrachloride extraction of a sample of haiari stem (No. 627), which gave no rotenone by ether extraction.

On the other hand, a sample of derris root (No. 412) whose ether extract yielded 2 to 3 per cent of amorphous material, in which no rotenone could be detected, gave neither crystalline nor amorphous material from a carbon tetrachloride extract. The ether extract of another sample of derris root (No. 548) deposited about 2 per cent of mixed amorphous and crystalline material which on examination was found to contain only a small proportion of rotenone, whereas only a fraction of 1 per cent of crystalline rotenone separated from the carbon tetrachloride extract.

Carbon tetrachloride will also be found superior to ether for extractions under tropical conditions because of its lower volatility.

Other Possible Extraction Methods

In an attempt to shorten the time of extraction, some experiments were made in which the root was extracted with solvents having a high solubility for rotenone, and the rotenone then crystallized from the dried extract by means of carbon tetrachloride. Acetone proved suitable for this purpose.

A derris sample (No. 594-B), yielding 6 per cent rotenone by the carbon tetrachloride method, also gave 6 per cent when extracted for 4 hours with acetone, followed by crystallization from carbon tetrachloride. A cubé root sample (No. 686-G), giving 6.3 per cent rotenone by the carbon tetrachloride method, gave about the same value when extracted for 4 hours with acetone and the rotenone crystallized from carbon tetrachloride. It is evident that acetone extracts the rotenone in a much shorter time than carbon tetrachloride, probably because it is a better solvent for the resinous material in which the rotenone may be incorporated.

However, the total material extracted by acetone amounts to more than that extracted by carbon tetrachloride. Consequently, in extractions such as the two just cited, a very considerable proportion of the dried acetone extract was insoluble in hot carbon tetrachloride. This necessitated filtration and numerous washings of the dried extract with hot carbon tetrachloride. The rotenone obtained in several tests made by this method was less pure, and, probably because of this, amounted to several tenths of a per cent more than that obtained by the carbon tetrachloride extraction method. This modified method thus has certain objections, although it may be useful when a rapid but approximate estimate of the rotenone content is desired.

Because of the high optical rotation of rotenone (in benzene $[\alpha]_D^{20°} = -224°$ for a 5 per cent solution) it was thought that a method for its determination might be based on this phenomenon. Extractions were made with such solvents as acetone, benzene, chloroform, and ethylene dichloride. The extracts were made to a definite volume, and the optical rotation was measured in a saccharimeter. By use of data previously obtained (*11*) the amount of rotenone represented by the rotation was calculated. The values obtained in this way for rotenone in two samples of derris root (Nos. 402 and 407) and one sample of cubé root (No. 584) were about twice those obtained by crystallization from ether or carbon tetrachloride. The optical rotation of an extract of one derris root (No. 412) indicated a content of over 5 per cent rotenone and that of another (No. 406) over 3 per cent, whereas neither of these samples gave any rotenone by crystallization from carbon tetrachloride extracts. The extract of one derris sample (No. 401) was dextrorotatory. Such erroneous values as the above may be expected, since there are numerous variable constituents of these extracts whose optical rotations are not known. It is thus evident that the optical rotation of the extract cannot be used as a measure of the amount of the rotenone present in the root.

Conclusions

The carbon tetrachloride extraction method outlined gives good results for the rotenone content of thoroughly air-dried derris roots, cubé roots, and haiari stems. The results of numerous extractions indicate that this method is superior to a similar method using ether.

The method gives correct or slightly high results for roots containing over 0.5 per cent rotenone. For roots containing 0.3 per cent rotenone or less the method is without value unless larger samples are used.

Acetone gives a more rapid extraction of the rotenone, but its complete separation from such extracts is difficult. Values based on the optical rotation of the extracts are incorrect.

A purely chemical method for the accurate determination of rotenone in plant materials is needed.

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New Reagent for Determination of Zinc

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ZINC is readily precipitated from an acid or a neutral solution by means of borneolglycuronic acid. Since this acid does not form insoluble salts with the other common metals, except cadmium, it offers an easy method not only for detecting zinc, but also for separating it from a mixture of other cations. Zinc in as low a concentration as 0.03 per cent will give a characteristic crystalline precipitate when treated with a 5 per cent aqueous solution of borneolglycuronic acid.

Zinc borneolglycuronate is a white glistening salt containing 2 molecules of water of crystallization.

Analysis. Calculated for $(C_{16}H_{25}O_7)_2Zn.2H_2O$: glycuronic acid, 51.1. Found: 50.8, 51.5.

The development of a simple and satisfactory quantitative method for zinc based on the precipitation of zinc borneolglycuronate is feasible and promising. The precipitate can be weighed directly, or it can be hydrolyzed by boiling with 1.0 *N* hydrochloric acid for 15 minutes. In this procedure, borneolglycuronic acid is split, and the glycuronic acid thus liberated can be determined by any of the common sugar methods, of which the Shaffer-Hartmann (*2*) is especially satisfactory. From the determined glycuronic acid, zinc can be calculated.

The reagent, borneolglycuronic acid, is best prepared by the method described by the writer (*1*). For the convenience of the reader, the essential details of the method are again outlined: Five grams of pulverized borneol are fed to a dog. The drug can be mixed directly with the food. The urine is collected for 24 hours, acidified, and treated with excess lead acetate to remove pigments. The precipitate is filtered off, and the filtrate heated to boiling. An excess of zinc acetate solution is added, and the precipitated zinc borneolglycuronate filtered off and washed with hot water until all coloring matter has been extracted.

To prepare borneolglycuronic acid, 100 grams of the zinc salt are dissolved in 140 cc. of hot 3.5 *N* sulfuric acid. The solution is rapidly cooled in ice and allowed to stand for several hours. The crystalline borneolglycuronic acid is filtered off and washed with cold water. One recrystallization from hot water is necessary to obtain a pure product.

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Determination of Nonmetallic Inclusions in Plain Carbon and Manganese Steels

Iodine and Nitric Acid Extraction Methods

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THIS method, using ferrous iodide solution for solution of the steel, has been developed from the procedure published by Eggertz (*3*). The formation of insoluble iron compounds is one of the chief obstacles in this method when applied to the determination of oxides in steel. The authors have found that the addition of a certain amount of ammonium citrate to the solution of ferrous iodide eliminates this difficulty. In addition, it has been found that the solubility of the oxides themselves is extremely small when the method is applied as described. Among the more recent investigators of iodine extraction methods are Westcott, Eckert, and Einert (*6*), who recommended the procedure for such inclusions as wrought iron slags, although no precautions were taken to prevent hydrolysis, and Willems (*7*) whose modified method resulted in the recovery of only 60 per cent of the manganese oxide.

Preparation of Ferrous Iodide Solution

Five grams of plain carbon steel drillings with silicon content not over 0.03 per cent are transferred to a 300-cc. Erlenmeyer flask containing 25 cc. of cold water, 4 grams of ammonium citrate, and 30 grams of pure iodine. The flask and its contents are twirled in ice water until the steel has practically all dissolved. Thirty grams of additional iodine are introduced, and the shaking is continued until all iodine has dissolved, at which time the solution is filtered. The total volume of the filtrate and washings should not exceed 75 cc. This amount of ferrous iodide is used to treat 5 grams of drillings or a 5-gram solid piece of steel. Should the drillings or solid piece treated weigh more than 5 grams, the ferrous iodide should be increased proportionately.

Solution of the Sample

From 5 to 10 grams of the carefully prepared drillings or solid piece of steel are treated with from 75 to 150 cc. of ferrous iodide solution in a 300-cc. Erlenmeyer flask. The stoppered flask is placed in ice water and twirled continuously. The solution should not be allowed to become warm at any time; therefore it is necessary that the agitation of the flask and its contents be continued until the sample has almost completely dissolved. The flask is then placed in a shaking machine (run at a low speed) until the metal has dissolved completely, at which time the solution is immediately filtered on an 11-cm. filter paper of close texture containing a small amount of ashless paper pulp. The filter paper and residue are washed from eighteen to twenty times with cold 2 per cent ammonium citrate solution to remove ferrous iodide, followed by hot 2 per cent ammonium citrate to remove all iodine, and ignited in a platinum crucible first at a low temperature and finally at 1000° C. in an oxidizing atmosphere, cooled in a desiccator, and weighed. If the silicon content of the steel exceeds 0.25 per cent, the residue is washed several times with hot water to remove ammonium citrate, after which it is washed with approximately 50 cc. of 5 per cent potassium hydroxide, then thoroughly with hot water, and ignited.

Determination of SiO_2, MnO, FeO, and Al_2O_3

The residue from the ferrous iodide extraction is fused with one gram (a sufficient amount) of sodium carbonate. The melt, after cooling, is transferred to a 150-cc. covered porcelain casserole, and dissolved in 20 cc. of hydrochloric acid (1 to 1). Five cubic centimeters of 60 per cent perchloric acid are introduced and the solution is evaporated to strong fumes of perchloric acid to dehydrate silica. The residue is treated with 50 cc. of water and a few drops of sulfurous acid; the solution is then heated to boiling to expel sulfur dioxide, and filtered on a 9-cm. paper containing some ashless paper pulp. The paper and silica are washed well with hot water, ignited at 1000° C., and weighed. The silica is then determined by volatilization with hydrofluoric and sulfuric acids in the usual manner.

The filtrate from the silica is diluted to exactly 100 cc. with water and divided into two equal portions. To one portion, contained in a 300-cc. Erlenmeyer flask, 15 cc. of nitric acid (sp. gr. 1.42) are added and the manganese is determined by the bismuthate-arsenite method. The manganese found is calculated to MnO.

To the other portion of the filtrate from the silica, contained n a 250-cc. beaker, 5 grams of ammonium chloride are added, and the solution heated to incipient boiling. Dilute filtered ammonium hydroxide (1 to 1) is added in faint excess (the pH value is held as near to 7 as possible), and the contents of the beaker are boiled for 30 seconds. The solution is filtered on a 9-cm. paper and the residue washed from eight to ten times with warm 2 per cent ammonium chloride solution. The filtrate is discarded. The precipitate is dissolved from the paper into the original 250-cc. beaker, with a jet of hot hydrochloric acid (1 to 1). The solution is nearly neutralized with ammonium hydroxide, 2 grams of ammonium chloride are added, and the contents of the beaker again heated to incipient boiling. The precipitation with ammonium hydroxide is then repeated, as described above. After filtering and washing with 2 per cent ammonium chloride solution, the paper and residue are transferred to a weighed platinum crucible provided with a tightly fitting cover, and ignited first at a low temperature and then to constant weight at 1100° C. The final heating should be done with the cover off or else some Fe_3O_4 will be formed. After cooling in a desiccator, the covered crucible and contents are weighed. The increase in weight represents $Fe_2O_3 + Al_2O_3$. The combined oxides of iron and aluminum are fused with one gram of sodium carbonate and the melt, after cooling, is dissolved in dilute hydrochloric acid. After boiling the solution for a few minutes to remove carbon dioxide, the iron and aluminum are precipitated with ammonium hydroxide, filtered, dissolved in hydrochloric acid, and the iron determined by reduction with stannous chloride and titration with potassium permanganate. The iron found is calculated to Fe_2O_3 and this weight is deducted from the combined weight of Fe_2O_3 and Al_2O_3, to give the weight of Al_2O_3. The weight of Fe_2O_3 found is calculated to FeO.

In case the actual determination of aluminum is desired, the precipitate from the second ammonium hydroxide separation, described above, is dissolved in 20 cc. of hydrochloric acid (1 to 3), the solution cooled to 10° C., and some ashless paper pulp added. The iron is precipitated by the addition, drop by drop with constant stirring, of a cold freshly prepared 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$). The presence of an excess of the reagent may be detected by the fact that the addition of more cupferron gives a snow-white precipitate which quickly dissolves. The precipitate is filtered on a 9-cm. paper and washed six to eight times with cold 2 per cent hydrochloric acid. The residue may be ignited and weighed as Fe_2O_3.

To the filtrate, which contains the aluminum, 30 cc. of nitric acid (sp. gr. 1.42) are added and the solution boiled down to a volume of 15 cc. Five cubic centimeters of perchloric acid are introduced and the contents of the beaker evaporated to dense fumes of perchloric acid. After cooling, the cover glass and sides of the beaker are rinsed down with a jet of water, and the solution is again evaporated to fumes of perchloric acid. Fifty cubic centimeters of water are introduced and the aluminum is precipitated with ammonium hydroxide, as already described. After igniting in a tared platinum crucible, provided with a closely fitting cover, the residue is weighed as Al_2O_3.

Table I

Slag	1 2 FeO.-SiO₂	2 2 MnO.-SiO₂	3 FeO.-MnO.SiO₂	4 FeO.-MnO.SiO₂	5 FeO.-MnO.SiO₂
	%	%	%	%	%
SiO_2	33.55	28.96	29.40	30.88	32.00
FeO	53.40	2.58	5.61	22.27	33.62
Fe_2O_3	6.23	...	11.17	8.29	12.29
MnO	...	63.15	49.11	33.44	16.79
	93.18	94.69	95.29	94.88	94.70
Fe (total)	45.79	2.01	12.17	23.11	34.73
Mn (total)	...	48.51	38.03	25.90	13.05

It will be noted that the most marked difference between the method as here described and the iodine methods formerly used consists in the addition of ammonium citrate (a neutral salt) and the low temperature maintained during the solution of the sample and the washing of the filter paper to remove ferrous iodide. It is essential to have the ammonium citrate present to prevent hydrolysis of iron. Samples analyzed in the absence of this salt give variable, erratic values for ferrous oxide, whereas, when the citrate is added, closely agreeing checks are obtained. The citrate also prevents the precipitation of ferric phosphate, thereby eliminating the necessity of testing for phosphorus. The temperature during solution of the steel is kept low further to insure the prevention of hydrolysis and especially to decrease the possibility of dissolving the inclusion particles. It may also be noted that the flask is agitated continuously during solution of the steel. Besides helping to keep the liquid cold, this prevents the formation of a film of carbon on the steel, which greatly retards the rate of solution. It may also be observed that the strength of the ferrous iodide solution is maintained within definite limits. Should the solution used be too weak, incomplete solution of carbides would ensue.

Sulfides are decomposed by the ferrous iodide treatment, the sulfur being set free as elemental sulfur. Nitrides are also decomposed. Some so-called plain carbon steels contain small amounts of chromium carbide and in some cases vanadium carbide. These carbides are not broken up by the ferrous iodide treatment, causing plus errors in any calculation of iron oxide from total oxides. However, it has been found in practice that these carbides, when present, are in such small quantities that their effect on the result is so slight that it may safely be neglected.

Experimental Data

Two grams of each of five 200-mesh slags, as shown in Table I, together with 5 grams of Armco iron drillings (on which a blank had been run), were treated as described.

Analyses of the slags after the treatment, together with the percentage recovery of the total silicon dioxide, iron, and manganese are given in Table II.

Table II

Slag	Analysis of Residue			Percentage of Total Recovered		
	SiO_2	Fe	Mn	SiO_2	Fe	Mn
	%	%	%	%	%	%
1[a]	32.80	45.51	...	97.8	99.4	...
2	27.93	1.96	47.78	96.4	97.5	98.7
3	28.72	12.01	37.60	97.7	98.7	98.9
4	30.22	23.09	25.85	97.9	99.9	99.8
5	31.41	34.45	13.11	98.1	99.2	99.0+

[a] To a mixture of slag 1 and Armco iron drillings, 0.01 gram of pure Al_2O_3 (finely powdered and ignited to 1600° C.) was added, and the whole treated by the ferrous iodide method. It was found that 0.0097 gram of Al_2O_3 was recovered.

Samples of steel containing 0.038 and 0.44 per cent sulfur, respectively, were treated with ferrous iodide and the residues were tested for sulfides with concentrated hydrochloric acid; no sulfides were detected. Fifty grams of steel were treated (in 10-gram portions) and the residues, after being centrifuged, were combined and analyzed for nitrogen; none was found. To a 5-gram sample of steel, 0.005 gram of phosphorus was added as ammonium phosphate, and the mixture treated with ferrous iodide; no phosphorus was found in the residue.

In order to test the accuracy and dependability of the method, a series of steel heats was made. Each heat was split, and one half was killed with aluminum according to the method of Herty, Freeman, and Lightner (*4*), while the other half was rapidly cooled. The aluminum-killed portions were analyzed for Al_2O_3 and the total oxygen was computed. The corresponding rapidly cooled portions were analyzed for slag inclusions by the ferrous iodide method and the total oxygen was calculated. Very close checks were obtained (*2*).

Determination of Al_2O_3 by Acid Extraction

This procedure is similar to that employed by Dickenson (*1*), except that the strength of the nitric acid is increased and the liquid is not aërated. It is recommended that this method be used for the determination of Al_2O_3, as the time required for solution of the steel is much less than that for solution in ferrous iodide, or in 20 per cent hydrochloric acid, as described by Kichline (*5*).

From 15 to 20 grams of the drillings or a solid piece of steel are treated with 600 to 800 cc. of 20 per cent nitric acid in a porcelain casserole. When all action has ceased the solution is filtered, with aid of gentle suction, on superimposed 11-cm. filter papers of close texture, containing a small amount of ashless paper pulp. The papers and residue are washed with 5 per cent hydrochloric acid to remove iron, and ignited in a platinum crucible. The contents of the crucible are fused with one gram (a sufficient amount) of sodium carbonate, and the aluminum is determined by one of the methods previously described.

A sample of steel containing a complex manganese-aluminum silicate gave a value of 0.007 per cent Al_2O_3 by both nitric acid and hydrochloric acid extraction. The ferrous iodide method, applied to the same sample, showed 0.0065 per cent Al_2O_3. Another steel yielded a value of 0.075 per cent Al_2O_3 by both the nitric acid extraction and the ferrous iodide treatment.

To a sample of alumina-free steel, 0.01 gram of Al_2O_3 (finely powdered and ignited at 1600° C.) was added. After applying this nitric acid extraction, 0.0095 gram of Al_2O_3 was recovered.

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Estimation of Gossypol in Cottonseed Meal

A Modified Method

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The Withers-Carruth method as modified by Schwartze and Alsberg for the estimation of gossypol in cotton seed is not adequate for the determination of gossypol in cottonseed meal. The proposed method has overcome the objections and consists in the removal of a part of the oil in the meal by a preliminary extraction with petroleum ether, followed by thorough extraction of gossypol from the air-dried meal with U. S. P. ethyl ether and removal of the ether from the extract by partial vacuum. The residual extract is diluted with petroleum ether and allowed to stand overnight. The material insoluble in petroleum ether precipitates and is filtered off. Aniline and ethylene glycol are added, the latter aiding the precipitation on the steam bath of the dianiline gossypol in the presence of a petroleum ether of high boiling point. After standing overnight, precipitates of a satisfactory degree of purity are obtained.

GOSSYPOL occurring in the cotton seed is readily soluble in ethyl ether. Carruth made use of this fact in his method of estimation (*2*). In the process of manufacture of cottonseed meal, the gossypol not expressed into the oil, but remaining in the meal, becomes in a large part insoluble in ethyl ether. In order to estimate the small amounts of this remaining ether-soluble gossypol in the meal, there is need of a method which is expeditious and accurate, and which will avoid the difficulties of the present method of Carruth as modified by Schwartze and Alsberg (*6*).

But one published modification of the Carruth method has been made, that of Schwartze and Alsberg. This consisted in extracting the ground seed in a Soxhlet extraction thimble, removing the ether, allowing the residue to stand overnight after the addition of 8 to 10 volumes of petroleum ether, and then filtering off the precipitated insoluble material that would otherwise contaminate the precipitate of dianiline gossypol. One cubic centimeter of aniline was then dissolved in the solution with shaking, and allowed to stand until precipitation occurred. After standing 3 to 7 days, this precipitate was filtered on a tared Gooch crucible, washed, dried at 100° C., and weighed. The filtrate was further allowed to stand from a week to a month in order to determine whether precipitation was complete. If necessary, corrections were made for any subsequent precipitation.

The accuracy of this method is shown by a recovery of 90 per cent of 0.7 gram of gossypol from 25 cc. of oil. In order to obtain this degree of accuracy, the authors used a large amount of gossypol in comparison with the minute amounts present in meal.

The Carruth method, as modified by Schwartze and Alsberg, is not sensitive enough to estimate the small amounts of ether-soluble gossypol remaining in the meal because of several factors. The excess oil in the oil–petroleum ether mixture hinders precipitation of dianiline gossypol. There is not a complete elimination of the troublesome contaminating insoluble precipitate (in petroleum ether); the length of time required to precipitate aniline gossypol and the incompleteness of this precipitation are unsatisfactory.

A study has been made of the factors involved in the estimation of the small amounts of the ether-soluble gossypol remaining in cottonseed meal, the results of which are presented in this paper. From this study the method was formulated for the estimation of gossypol.

The modifications introduced are: a preliminary extraction of the oil remaining in the meal; the precipitation upon standing overnight and filtering off an insoluble flocculent precipitate; the use of ethylene glycol as an aid in precipitation of gossypol as dianiline gossypol; and digestion on the steam bath in the presence of a high boiling point petroleum ether, followed by constant shaking or standing before the precipitation of dianiline gossypol is complete, when it is filtered off, dried, and weighed.

METHOD IN DETAIL

PRELIMINARY EXTRACTION OF OIL[1]

Transfer a charge of 75 grams of cottonseed meal, ground to pass through a 40-mesh sieve, to a 500-cc. Erlenmeyer flask with 100 cc. of petroleum ether (b. p. 30° to 80° C.). (Fractions of ordinary gasoline distilling between 30° and 108° C. have been used.) Shake vigorously for 5 minutes and filter through a Büchner funnel. Remove thoroughly with a small amount of petroleum ether any meal adhering to the Erlenmeyer flask. Carefully remove the petroleum ether from the meal in the Büchner funnel. Transfer the meal to shallow pans, and allow to dry at room temperature for several hours with occasional stirring in order to remove all the petroleum ether.

After washing with petroleum ether and air-drying, extract the charge thoroughly (approximately 72 hours) with U.S.P. ethyl ether to which 5 cc. of distilled water are added in the receiving flask, using a Soxhlet extractor having an inside diameter of 50 mm. (Anhydrous ether and moisture-free samples of meal cannot be used as the gossypol does not extract quantitatively.) After removing the thimbles, recover the ether by distillation into the Soxhlet until 15 to 20 cc. of extract remain in the extraction flask. Remove the

[1] Omit this step in the analysis of *seed*, to prevent the precipitation of gossypol by the petroleum ether; however, the small amounts of gossypol present in the *meal* do not precipitate.

flask and filter the extract through a Gooch crucible into a 250-cc. Erlenmeyer flask placed under a bell jar. Wash the residue with ethyl ether. The ether is distilled off rather completely under reduced pressure, and this is facilitated by placing the flask containing the filtrate in a beaker of warm water. (The ether extract is readily injured, detected by a burnt odor, if heated strongly on the steam bath.) Then add to the filtrate 75 cc. of petroleum ether of a high boiling point (65° to 110° C.), and let the flask stand overnight. The following morning filter the solution through a Gooch crucible in order to remove the material precipitated by the petroleum ether. Wash the precipitate with petroleum ether, combining the washings with the filtrate.

Add 5 cc. of ethylene glycol (c. p. or practical, Eastman) and 2 cc. of aniline to the filtrate, thoroughly mix by shaking, and digest gently on the steam bath 1 to 2 hours. When the digestion is discontinued, replace the petroleum ether lost to give a total volume of 60 to 75 cc. Allow the flask to cool, stopper, and let stand overnight. (Longer standing is necessary for precipitates of gossypol smaller than the usual amounts.) Filter through a tared Gooch crucible and wash the precipitate of dianiline gossypol with petroleum ether (b. p. 30° to 80° C.). Follow by four washings with water and then with a few cubic centimeters of petroleum ether. Dry the precipitate to constant weight at 100° C. In converting the dianiline gossypol to gossypol, multiply by the factor 0.775.

Preparation of Purified Gossypol

In order to study the factors involved in the proposed method for the estimation of gossypol, a supply of purified gossypol was necessary. This was prepared from the seed by the method of Clark (*5*), in which the ground seed is percolated for 3 hours with ether sufficient to yield 3 liters of extract per kilogram of seed. The ether is recovered by distillation, and the residue is filtered through activated carbon. The filtrate is dissolved in an equal volume of petroleum ether and then treated with the same volume of glacial acetic acid. Crystallization begins at once, and the process is complete within a few hours.

Some difficulty was experienced in obtaining the gossypol acetate (gossypol combined with one molecule of acetic acid of crystallization) precipitate from the extracted oil from fresh seed. Removal of the ether from the extracted oil by distillation on a steam bath injures the extract (it has a burnt odor) so that the gossypol will not readily precipitate upon the addition of glacial acetic acid. The ground seed was percolated with ether. The resulting oil-ether mixture was freed from ether by gently heating at a temperature which did not rise above 60° C. This was done by immersing in the solution an electric heater consisting of a coil of Nichrome wire, No. 20, 12.5 feet (31.8 cm.) long having a resistance of 25 ohms (suggested by E. P. Clark).

The crude gossypol was recrystallized three times as the acetate from a mixture of ethyl ether and ethylene chloride (4 to 1) and a volume of glacial acetic acid equal to one-half the volume of the mixture. There is present a reddish impurity which is readily soluble in this mixture. The gossypol was then further purified free of any reddish color by the method of Clark (*3*, p. 731), and solvent-free gossypol was prepared by crystallizing the purified substance from ether (*3*, p. 733).

The final product of purified gossypol was of a bright yellow color.

Influence of Ethylene Glycol on Precipitation of Dianiline Gossypol

Without heat or agitation dianiline gossypol precipitated more completely from a petroleum ether solution of crude cottonseed oil upon the addition of 5 cc. of ethylene glycol in the presence of aniline. Comparisons were made by dissolving definite amounts of purified gossypol in 5 cc. of refined cottonseed oil and 50 cc. of petroleum ether, adding aniline to all determinations and 5 cc. of ethylene glycol. After thorough shaking and standing, those determinations containing the ethylene glycol began to precipitate in a short time. Those determinations not containing ethylene glycol, however, on further standing after filtering off the precipitate, gave an additional small amount of precipitate. The total yield of gossypol was not so great as where ethylene glycol was added. The results are given in Table I.

Table I. Influence of Ethylene Glycol upon Recovery of Relatively Large Amounts of Gossypol without Heat or Constant Agitation

(Gossypol dissolved in 5 cc. of oil, 25 cc. of petroleum ether, and precipitated with 2 cc. of aniline)

Detn.	Gossypol Taken	Aniline Gossypol Weighed	Gossypol Recovered		Days Stood	Remarks
	Mg.	*Mg.*	*Mg.*	%		
(*a*) Method of Schwartze and Alsberg without use of ethylene glycol						
1	48.8	49.5	38.4	78.7	2	
2	48.8	48.3	37.5	76.8	2	Slow and incomplete precipitation
3	25.0	24.6	19.1	76.4	2	
4	25.0	26.4	20.5	82.0	2	
5	25.0	27.0	20.9	83.6	2	
			Av.	79.5		
(*b*) With 5 cc. of ethylene glycol, other reagents as above						
6	48.8	57.3	44.4	91.0	1	
7	48.8	58.7	45.5	93.2	1	More complete precipitation
8	48.8	55.8	43.3	88.7	1	
9	48.8	56.9	44.1	90.4	1	
10	48.8	58.1	45.1	92.4	1	
11	48.8	58.3	45.2	92.6	1	
			Av. 44.6	91.4		

Ethylene glycol is not miscible with the oil–petroleum ether solution, but in the presence of this reagent the precipitation of gossypol is facilitated. It has been found that 10 mg. of gossypol dissolved in refined cottonseed oil can be recovered quantitatively from the oil by repeated extractions with ethylene glycol when approximately 40 mg. of anhydrous sodium carbonate are used together with 75 cc. of petroleum ether. If water is present, troublesome emulsions are encountered. The gossypol is also unstable in the presence of aqueous alkaline solutions.

Aniline is readily soluble in ethylene glycol and much less soluble in the cottonseed oil–petroleum ether mixture, and it thus appears that gossypol and aniline are intimately brought together in the ethylene glycol layer where precipitation occurs. Therefore, agitation should hasten precipitation. This will be considered later.

The favorable influence of ethylene glycol on precipitation resulted in an average of 91.4 per cent recovery of 48.8 mg. of gossypol. This is 11.9 per cent greater than by the method of Schwartze and Alsberg, in which the precipitation took twice as long.

Precipitation of Small Amounts of Gossypol

The amounts of gossypol in Table I are not comparable to the small amounts determined in cottonseed meal, so it appeared desirable to determine whether such amounts as are estimated in meal could be precipitated in the presence of 2 cc. of refined cottonseed oil with the aid of ethylene glycol. The amount of the other reagents was the same as given in Table I. They were well mixed by shaking by hand, and then allowed to stand in a refrigerator at about 10° C. until precipitation was complete. The dianiline gossypol began to precipitate on standing overnight. Details are given in Table II.

The results show that 4 of the 5 mg. of gossypol dissolved in the oil were recovered after standing 8 days at approximately 10° C., and that 8.7 of 10 mg. were recovered after standing 13 days. This precipitation is complete enough for

the estimation of gossypol in cottonseed meal. In a charge of 75 grams of meal, 1 mg. of gossypol not recovered is equivalent to 0.0013 per cent, which is not significant.

TABLE II. RECOVERY OF SMALL AMOUNTS OF GOSSYPOL WITHOUT HEAT

Detn.	Gossypol Taken	Aniline Gossypol Weighed	Gossypol Recovered		Days Stood	Remarks
	Mg.	*Mg.*	*Mg.*	%		
			(*a*) WITHOUT AGITATION[a]			
1	5.0	5.3	4.1	82.0	8	
2	5.0	5.6	4.3	86.0	8	
3	5.0	5.8	4.5	90.0	8	Stood in cooler
4	5.0	4.9	3.8	76.0	8	at 10° C.;
5	5.0	4.8	3.7	74.0	8	precipita-
6	5.0	4.7	3.6	72.0	8	tion delayed
7	5.0	5.1	4.0	80.0	8	
8	5.0	5.5	4.3	86.0	8	
		Av.	4.0	80.7		
			(*b*) WITH AGITATION[b]			
9	10.0	11.3	8.8	88.0	13	Stood in cooler
10	10.0	11.8	9.2	92.0	13	13 days at
11	10.0	10.6	8.2	82.0	13	10° C.;shaken
						24 hours; pre-
		Av.	8.7	87.3		cipitation de-
						layed

[a] Five mg. of gossypol were dissolved in 2 cc. of oil, 25 cc. of petroleum ether, 2 cc. of aniline, and 5 cc. of ethylene glycol.
[b] With 10 mg. of gossypol in 2 cc. of oil and 75 cc. of petroleum ether, other reagents as given above.

EFFECT OF HEAT AND AGITATION UPON PRECIPITATION

The results in Table II show good recovery of gossypol upon long standing. In order to hasten precipitation, the effect of heat was tried by digesting several determinations of 10 and 25 mg. of gossypol 2.5 hours on the steam bath. The gossypol was dissolved in 2 cc. of oil to which were added 5 cc. of ethylene glycol, 2 cc. of aniline, and 50 cc. of petroleum ether of a high boiling point, as suggested by E. P. Clark. After the digestion, the cooled, stoppered flasks were mechanically agitated continuously for 48 and 72 hours. The mechanical shaker was similar in type to the Camp shaking apparatus. It was driven by a water motor making 50 to 60 revolutions per minute. The beneficial effect of heat in hastening precipitation is shown in Table III.

TABLE III. EFFECT OF DIGESTION AND AGITATION UPON RECOVERY OF GOSSYPOL

(In presence of 2 cc. of oil, 50 cc. of petroleum ether,[a] 2 cc. of aniline, and 5 cc. of ethylene glycol)

Detn.	Gossypol Taken	Aniline Gossypol Weighed	Gossypol Recovered		Hours Shaken	Remarks
	Mg.	*Mg.*	*Mg.*	%		
1	10.0	10.8	8.4	84.0	48	Shaking and
2	10.0	10.8	8.4	84.0	48	heat aided
3	10.0	10.8	8.4	84 0	48	precipita-
4	10.0	11.0	8.5	85.0	48	tion
		Av.	8.4	84.1		
5	25.0	29.5	22.9	91.6	72[b]	Shaking and
6	25.0	30.0	23.3	93.2	72	heat help-
7	25.0	29.1	22.6	90.4	72	ful as
8	25.0	30.3	23.5	94.0	72	above
		Av.	23.1	92.3		

[a] Boiling point 65° to 110° C.
[b] After shaking 24 hours, precipitates appeared ready to filter.

With 2.5 hours of digestion and 48 hours of shaking, 8.4 of 10 mg. of gossypol (Table III) were recovered. Likewise 23.1 of 25 mg. of gossypol were recovered by the same procedure. But without the aid of heat, the precipitation of gossypol was delayed so that a similar amount of 8.7 mg. of gossypol (Table II, *b*) was recovered after standing 13 days at 10° C. and with a final shaking of 24 hours.

EFFECTS OF COTTONSEED OIL ON PRECIPITATION OF GOSSYPOL AS DIANILINE GOSSYPOL

Small amounts of gossypol are not readily precipitated from large volumes of refined cottonseed oil. This has been shown by Carruth (*2*), who found that not more than 90 per cent of 0.5 gram of gossypol was recovered from 50 cc. of oil, thus leaving approximately 50 mg. in solution. Likewise, Schwartze and Alsberg (*6*) recovered approximately 90 per cent of 0.7 gram of gossypol in 25 cc. of refined oil, 70 mg. remaining in solution. Although the amount of oil and gossypol used by these investigators is more than is obtained from a charge of 75 grams of cottonseed meal, yet it is found that less gossypol remains in solution or is not precipitated by the reagents in the proposed method, when proportional amounts of oil are used.

TABLE IV. EFFECT OF PRESENCE OF OIL ON PRECIPITATION OF GOSSYPOL

(Two cc. of aniline and 5 cc. of ethylene glycol added to each determination)

Detn.[a]	Gossypol Taken	Oil	Petroleum Ether	Aniline Gossypol Weighed	Gossypol Recovered		Remarks
	Mg.	*Cc.*	*Cc.*	*Mg.*	*Mg.*	%	
1	5.0	2	25	5.1	3.95	79.0	Some precipi-
2	5.0	2	25	5.3	4.11	82.5	tate on first
3	5.0	2	25	5.8	4.50	90.0	and second
4	5.0	2	25	5.7	4.42	88.4	days, con-
							siderable in
				Av.	4.25	84.9	3 days
5	5.0	5	25	0.5	0.39	7.8	No precipi-
6	5.0	5	25	1.3	1.01	20.2	tate on first
7	5.0	5	25	0.8	0.62	14.4	day; slight
8	5.0	5	25	0.7	0.54	10.8	on third day
				Av.	0.64	13.3	
9	10.0	2	75	11.8	9.15	91.5	Precipitation at
10	10.0	2	75	11.9	9.22	92.2	once;copious
11	10.0	2	75	11.0	8.53	85.3	by third day
12	10.0	2	75	12.1	9.38	93.8	
				Av.	9.07	90.7	
13	10.0	5	75	10.6	8.23	82.3	Slight pre-
14	10.0	5	75	11.6	8.99	89.9	cipitate on
15	10.0	5	75	10.9	8.45	84.5	first day;
16	10.0	5	75	10.3	7.98	79.8	precipitating
							slowly on
				Av.	8.41	84.1	third day

[a] All determinations stood 8 days in an electric refrigerator at 10° C.

The data presented in Table IV show the influence of 2 and 5 cc. of refined cottonseed oil, respectively, on the precipitation of 5 and 10 mg. of gossypol, other factors remaining the same. An inspection of determinations 1 to 8, using 5 mg. of gossypol, shows that in the presence of the larger amount of oil, the precipitation of dianiline gossypol is materially slowed up, and that the recovery is much less, 13.3 per cent compared to 84.9 per cent. Also, when 10 mg. of gossypol are used, recovery is quicker and better in the presence of 2 cc. rather than 5 cc. of refined oil (determinations 9 to 16) with 93.8 per cent recovered compared to 84.1 per cent.

Table V presents additional data in support of the effect of 5 cc. of oil on the recovery of 5, 10, and 15 mg. of gossypol (determinations 1 to 10) compared to the recovery of 5, 10, and 25 mg. of gossypol in the presence of 2 cc. of oil, obtained in previous results (Tables II and III). In every case the average results of the amounts of gossypol recovered are higher in the presence of less oil, 2 cc. compared to 5 cc. Thus, in determinations 1 to 3, an average of 59.3 per cent of 5 mg. of gossypol is recovered in the presence of 5 cc. of oil, compared to 80.7 per cent in the presence of 2 cc. of oil. Likewise, in determinations 4 to 7, an average of 78 per cent of 10 mg. of gossypol is recovered in the presence of 5 cc. of oil, in comparison with 84.1 per cent when 2 cc. of oil were used. Also, in determinations 8 to 10, 83.1 per cent of 15 mg. of gossypol was recovered with 5 cc. of oil, in comparison to 92.3 per cent when 2 cc. of oil were used.

The purpose in the proposed method of the preliminary extraction of a part of the oil from the cottonseed meal with petroleum ether is to eliminate this somewhat troublesome factor. Approximately 2 cc. of oil are left in the charge; residues yielding as high as 5 cc. of oil are to be avoided. This

extraction did not remove a detectable quantity of gossypol, as shown by shaking the extract with ethylene glycol and anhydrous sodium carbonate in which the gossypol is more readily soluble. No gossypol could be precipitated from the petroleum ether extract as the dianiline compound.

Table V. Effect of Oil or Oil and Digestion on Precipitation of Gossypol in Presence of 5 cc. of Aniline and of Ethylene Glycol

Detn.	Gossypol Taken	Aniline Gossypol Weighed	Gossypol Recovered		Days Stood	Remarks
	Mg.	*Mg.*	*Mg.*	%		
(*a*) precipitated without digestion in presence of 5 cc. of oil and 75 cc. of petroleum ether						
1	5.0	3.4	2.6	52.0	50	Precipitation incomplete
2	5.0	4.7	3.6	72.0	50	
3	5.0	3.5	2.7	54.0	40	
		Av.	3.0	59.3		
1–8, Table II	5.0	Av.	4.0	80.7	8	2 cc. each of oil and aniline, and 25 cc. of petroleum ether used
(*b*) digested with 50 cc. of petroleum ether, 5 cc. of oil, and 2 cc. of aniline; other reagents as above					Shaken	
4	10.0	9.6	7.4	74.0	8	
5	10.0	10.2	7.9	79.0	6	
6	10.0	10.6	8.2	82.0	6	
7	10.0	9.9	7.7	77.0	6	
		Av.	7.8	78.0		
1–4, Table III	10.0	Av.	8.4	84.1	2	2 cc. of oil used
8	15.0	15.7	12.2	81.3	2	
9	15.0	16.3	12.6	84.0	2	
10	15.0	16.3	12.6	84.0	2	
		Av.	12.5	83.1		
5–8, Table III	25.0	Av.	23.1	92.3	3	2 cc. of oil used

Effect of Ethyl Ether on Precipitation

It is desirable to know whether it is necessary to remove the small amount of residual ether in the ethyl ether extract of cottonseed meal in order to obtain complete precipitation of the gossypol. The effect was studied of the influence of 0.5 and of 1.0 cc. of ether upon precipitation of 10 mg. of gossypol dissolved in 2 cc. of refined oil, with the other reagents present in the amounts given in the method. The results are presented in Table VI.

Table VI. Effect of Ethyl Ether upon Recovery of Small Amounts of Gossypol without Digestion

(In 2 cc. of oil, 2 cc. of aniline, 75 cc. of petroleum ether, and 5 cc. of ethylene glycol)

Detn.	Ethyl Ether Used	Gossypol Taken	Aniline Gossypol Weighed	Gossypol Recovered		Days Stood	Remarks
	Cc.	*Mg.*	*Mg.*	*Mg.*	%		
1	0.5	10.0	11.8	9.2	92.0	15	All detns. shaken 10 hours before filtering
2	0.5	10.0	10.5	8.1	81.0	15	
3	0.5	10.0	11.2	8.7	87.0	15	
			Av.	8.7	86.7		
4	1.0	10.0	10.4	8.1	81.0	15	
5	1.0	10.0	10.2	7.9	79.0	15	
6	1.0	10.0	10.3	8.0	80.0	15	
			Av.	8.0	80.0		

The results of determinations 1 to 3 show that 8.7 of 10 mg. can be recovered in the presence of 0.5 cc. of ethyl ether. This is the same amount which was recovered from 10 mg. of gossypol in determinations 9 to 11 (Table II). One cubic centimeter of ethyl ether does appear to lower the per cent recovered slightly (80 versus 87 per cent without ethyl ether). However, when expressed in milligrams of gossypol, this difference is of doubtful significance.

Because dianiline gossypol is slightly soluble in ether, the residual ether in the extract should not exceed one cc. In order to prevent overheating of the extract, the ether is removed under reduced pressure.

The results show that amounts of ether as small as 0.5 cc. do not interfere with the precipitation of dianiline gossypol.

Solubility of Dianiline Gossypol in Reagents

The solubility of dianiline gossypol was determined in the reagents used in this method of estimation. Weighed amounts of dianiline gossypol which had been recrystallized from boiling benzene were agitated from 5 to 9 days at laboratory temperature in the presence of the various reagents. The undissolved dianiline gossypol was filtered off, dried, and weighed. The results are given in Table VII.

Table VII. Solubility of Dianiline Gossypol in Reagents

Detn.	Aniline Gossypol Taken	Aniline Gossypol Recovered	Gossypol Dissolved	Equiv. Gossypol Dissolved	Days Shaken	Temp.
	Mg.	*Mg.*	*Mg.*	*Mg.*		° *C.*
two cc. of oil, 2 cc. of aniline, 5 cc. of ethylene glycol, and 75 cc. of petroleum ether[a]						
1	25.1	21.9	3.2	2.5	5	23 to 26
2	25.5	23.2	2.3	1.8	5	
3	26.7	23.7	3.0	2.3	5	
4	25.8	22.9	2.9	2.2	5	
5	25.6	22.8	2.8	2.2	5	
			Av. 2.8	2.2		
two cc. of oil and 75 cc. of petroleum ether						
6	10.0	8.4	1.6	1.2	6	
7	10.0	8.8	1.2	0.9	6	
			Av. 1.4	1.1		
five cc. of oil and 75 cc. of petroleum ether						
8	25.0	23.7	1.3	1.0	5	
9	25.0	23.6	1.4	1.1	5	
10	25.0	24.1	0.9	0.7	5	
			Av. 1.2	0.9		
two cc. of oil, 5 cc. of glycol, and 75 cc. of petroleum ether						
11	11.4	10.8	0.6	0.5	9	23 to 25
12	11.5	10.6	0.9	0.7		
13	10.0	8.4	1.6	1.2		
14	10.1	8.2	1.9	1.5		
15	11.3	9.9	1.4	1.1		
Av.	10.86	9.58	1.28	1.0		
one hundred cc. of petroleum ether						
16	25.3	25.1	0.2	0.2	9	23 to 25
17	25.5	24.9	0.6	0.5		
18	26.5	25.5	1.0	0.8		
Av.	25.8	25.2	0.6	0.5		

[a] Boiling point 30° to 80° C.

The results of determinations 1 to 5 show that 2.8 mg. of dianiline gossypol (2.2 mg. of gossypol) are dissolved in the reagents used in the method. These results compare favorably with the amounts not recovered in studying the influence of the various factors in the method. The solubility of dianiline gossypol in the reagents, when some of the reagents are omitted, varies, but this is less than the solubility in all of the reagents.

In 100 cc. of petroleum ether, the dianiline gossypol is soluble to the extent of one-half of the amount soluble in the reagents prescribed by the method when using 75 cc. of petroleum ether, 2 cc. of oil, and 5 cc. of ethylene glycol. Small amounts of dianiline gossypol are soluble in aniline, especially with increase in temperature. The dissolved dianiline gossypol was calculated to its equivalent in gossypol in order to compare these results with the amounts not recovered in studying the effects of heat, agitation, and oil on precipitation (Tables III and IV). The amount which dissolved in the reagents agrees closely with the amounts not recovered (Table VIII).

The small loss or incomplete recovery of gossypol (Table VIII) is largely accounted for by the solubility of dianiline gossypol in the reagents. The small discrepancies in the results may be due to slight changes in temperature at which the determinations were made, although they are within the limits of the experimental error of the method.

Table VIII. Gossypol Dissolved and Not Recovered by Method

Table No.	Av. of Detns.	Gossypol Dissolved	Remarks
		Mg.	
VII	1 to 5	2.2	Dissolved
III	1 to 4	1.6	Not recovered, effect of heat and agitation
III	5 to 8	1.9	Not recovered, effect of heat and agitation
V	4 to 7	2.2	Not recovered, effect of oil and digestion
V	8 to 10	2.5	Not recovered, effect of oil and digestion

In the recovery of small amounts of gossypol, an average of one mg. not recovered in determinations 1 to 8 agrees with the solubility figures shown in Table VIII as well as could be expected when it is observed that only one-third as much petroleum ether was used in these determinations and that the refrigerator temperature where they stood was much lower than that in the laboratory. In this case an average of one mg. was not recovered, whereas in determinations 9 to 11 (Table II) with 75 cc. of petroleum ether, the amount was 1.3 mg.

Purity of Dianiline Gossypol Precipitate

The nitrogen content of the dianiline gossypol is an indication of the degree of its purity. Clark (*4*) calculated this to be 4.19 per cent. He reported duplicate results of 4.12 and 4.14 per cent on a purified sample of dianiline gossypol. The nitrogen content was determined on a sample of dianiline gossypol recrystallized from boiling benzene, and in precipitates obtained from cottonseed meal. Mercury was used as the catalyst in the micro-Kjeldahl method adapted from Pregl for the determination of nitrogen. Ammonium sulfate and urea served as controls on the accuracy of the method. The results obtained from dianiline gossypol are shown in Table IX.

Table IX. Nitrogen Content of Dianiline Gossypol

Detn.	Aniline Gossypol Taken	0.04 *N* Acid	Nitrogen	
	Mg.	*Cc.*	*Mg.*	%
		Recrystallized from boiling benzene		
1	81.2	5.79	3.242	3.99
2	80.2	5.81	3.254	4.06
3	80.3	5.87	3.298	4.11
4	80.5	5.78	3.237	4.02
5	80.0	5.82	3.259	4.07
			Av.	4.05[a]
		From cottonseed meal		
6	32.9	2.25	1.260	3.83
7	98.0	6.71	3.758	3.83
8	102.5	6.83	3.825	3.73
9	87.3	6.24	3.494	4.00
10	39.5	3.02	1.691	4.28
11	41.4	3.14	1.753	4.23
12	21.7	1.60	0.896	4.13
13	26.5	1.99	1.114	4.20
14	87.4	6.28	3.517	4.02
15	49.2	3.76	2.106	4.28
16	93.2	6.79	3.802	4.08
17	112.4	7.35	4.116	3.66
18	32.9	2.42	1.355	4.12
19	62.7	4.22	2.363	3.77
20	53.6	3.89	2.178	4.06
			Av.	4.01

[a] Theoretical amount calculated by Clark, 4.19%.

The nitrogen content of dianiline gossypol recrystallized from boiling benzene averaged 4.05 per cent (3.99 to 4.11), and thus agrees fairly closely with the theoretical nitrogen content of 4.19 per cent when it is considered that the dianiline gossypol was recrystallized but once.

The precipitates of dianiline gossypol obtained from the determinations of ether-soluble gossypol in cottonseed meal showed more variation in nitrogen content, an average of 4.01 per cent (3.66 to 4.28). This variation, however, is only slightly greater than reported by Schwartze and Alsberg (3.75 to 4.04) in the aniline gossypol obtained from seed. Carruth (*1*) reported results varying between 3.97 and 4.84 per cent nitrogen. Some of his precipitates which contained the greater amounts of nitrogen may have occluded free aniline.

The variation in nitrogen content from the theoretical, as observed in the above precipitates (Table IX), is not great. These results show that the precipitates obtained from cottonseed meal by the proposed method consist of dianiline gossypol of a fair degree of purity. In fact, the method gives clean, uniform precipitates of definite crystalline structure.

Estimation of Gossypol in Cottonseed Meal by Proposed Method

It was desirable to know what results could be obtained from meals with unlike gossypol content. These results are presented in Table X. One meal contained a comparatively high content of gossypol, whereas the other was relatively low, only 13.8 per cent as much as the former.

Table X. Results of Estimation of Gossypol in Cottonseed Meal by Proposed Method

Detn.	Sample[a]	Aniline Gossypol	Gossypol	
		Gram	*Gram*	%
		With 48 hours' extraction		
1	1421	0.0971	0.0675	0.0450
2	1421	0.0890	0.0690	0.0460
3	1421	0.0954	0.0740	0.0493
4	1421	0.0874	0.0678	0.0452
5	1421	0.0932	0.0723	0.0482
		Av.	0.0701	0.0467
		With 72 hours' extraction		
6	1421	0.0980	0.0760	0.0507
7	1421	0.1025	0.0795	0.0530
		Av.	0.0777	0.0519
		With 48 hours' extraction		
8	1414	0.0114	0.0088	0.0059
9	1414	0.0126	0.0098	0.0065
10	1414	0.0137	0.0106	0.0071
		Av.	0.0097	0.0065

[a] Charge, 150 grams.

The results of determinations 1 to 5 by this method are consistent, the maximum variation being 0.004 per cent. Determinations 6 to 8 of cottonseed meal No. 1414 gave an average of 0.0065 per cent. The results show that the method is applicable to meals containing very small amounts of gossypol.

It is also seen that 72 hours of Soxhlet extraction of the meal gave 0.005 per cent more gossypol than 48 hours.

It was found that air-dried samples of meal and U. S. P. grade of ethyl ether (from J. T. Baker Chemical Co.) should be used. Gossypol is extracted with great difficulty after the meal has been dried in vacuum with or without heat or over calcium chloride in a desiccator. Also anhydrous ether was not so efficient as U. S. P. ether in extracting gossypol from air-dried meal (0.0399 against 0.0701 gram) and gave even poorer results on moisture-free meals.

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Effect of Reversion Products and Amino Compounds on Sucrose Determinations in Cane Products

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During the years 1924 to 1930 the associate referee on polariscopic methods of the Association of Official Agricultural Chemists, assisted by various collaborators, made a critical comparative study of several modern methods of sucrose determination by double polarization (*7*). The solutions analyzed contained known amounts of sucrose in mixture with invert sugar, reversion products of invert sugar, amino compounds (asparagine and aspartic acid which are the principal substances of this nature found in cane products, *8*), and salts.

The four inversion methods employed were: (*a*) the official invertase method of the A. O. A. C. (*2*); (*b*) Jackson and Gillis method II (*5*); (*c*) Jackson and Gillis method IV (*6*); and (*d*) Schrefeld's modification of Herzfeld's plain acid method (*3*). The inversions were carried out mostly at room temperature, but in some of the work higher temperatures were employed: 55° C. in method *a;* 60° C. in methods *b* and *c;* and 67° to 69.5° C. in method *d*.

The results of these investigations may be summarized briefly as follows:

1. The solution used for the direct polarization must have the same dry-substance concentration as the solution used for inversion.
2. The Clerget divisor must be based on the dry-substance concentration, and not on the sucrose concentration or on the invert reading alone.
3. It is preferable whenever possible to carry out the inversions at room temperature, because at high temperatures slight variations in the time used may have an appreciable effect on such reactions as the destruction of invert sugar in the presence of strong acid, on the hydrolysis of inversion products, and on the interaction between invert sugar and amino compounds.
4. The invertase method is the only one of the four methods compared which may be depended upon to give reliable sucrose results.
5. The sucrose result by Jackson and Gillis method II is increased by reversion products hydrolyzed under the conditions of the analysis.
6. The sucrose result by Jackson and Gillis method IV is increased by the hydrolysis of the reversion products in the same way as in method II. But aspartic acid or asparagine lowers the sucrose result considerably.
7. Accordingly, the difference between the sucrose result by Jackson and Gillis method II and that by the invertase method gives a relative measure of the reversion products hydrolyzed by hydrochloric acid under the conditions of the analysis.
8. The difference between the sucrose result by Jackson and Gillis method II and that by method IV gives a relative measure of the amino compounds present.
9. The plain acid method may give any kind of result, high, low, or correct within the limits of error, depending on the relative proportions of levulose, reversion products, and amino compounds present.
10. In the case of mixtures of known amounts of sucrose with a practically sucrose-free low-purity product, containing 13.74 per cent ash on the basis of dry substance, the salts as such had no noticeable effect on the Clerget divisor for any of the four methods investigated, provided the divisor was based on the dry-substance concentration.

The same four methods which had been applied to artificial mixtures containing known quantities of sucrose have now been used in the analysis of various blackstraps and refinery sirups. In order to obtain strictly comparable results, only one solution containing several normal weights was prepared, clarified with dry lead subacetate, and filtered. For the invertase method, a portion of the filtrate was deleaded with dry ammonium dihydrogen phosphate, and equal parts of the final filtrate, each containing 6.5 grams of product in 100 ml. of final volume, were used for the direct reading and for the inversion. The portions used for the three acid hydrolysis methods were prepared in the same way except that dry potassium oxalate was employed as a deleading agent. The inversions were carried out at a temperature of 26° to 30° C., and the polariscope readings were made at the standard temperature of 20° C.

The results, calculated in accordance with rules 1 and 2 given above, are shown in Table I.

Table I. Comparison of Sucrose Found by Four Clerget Methods

Sample	Invertase	J. & G. Method II	J. & G. Method IV	Plain Acid Method
	%	%	%	%
		Filtered sirups		
1	30.65	31.51	30.96	31.02
2	38.17	38.71	38.50	38.55
3	37.82	38.85	38.19	38.26
4	35.56	36.59	36.48	36.70
5	33.13	33.73	33.61	33.81
6	29.94	30.26	29.97	30.19
7	38.29	38.39	38.14	38.19
8	35.11	35.39	35.27	35.18
Av.	34.86	35.43	35.14	35.24
		Refinery blackstraps		
9	35.84	37.12	36.34	36.30
10	32.80	34.19	33.79	34.00
11	31.72	33.02	32.46	32.84
12	34.26	35.58	34.69	34.94
13	34.65	35.29	34.71	34.62
14	30.76	31.55	31.11	31.97
Av.	33.34	34.46	33.85	34.11
		Raw sugar blackstraps		
15	33.28		33.65	33.68
16	30.55		31.03	31.28
17	33.30		34.06	34.14
18	34.16		34.36	34.58
19	31.91		31.80	31.94
20	30.76		31.04	31.30
21	35.47		36.46	36.81
22	40.59		41.63	41.65
23	32.80		33.05	33.08
Av.	33.65		34.12	34.27

Unfortunately, Jackson and Gillis method II could not be used on the raw sugar blackstraps because the inverted solutions turned so dark upon neutralization with ammonia that they could not be read accurately even with a half-shadow angle of 15 degrees. However, in the two series where Jackson and Gillis method II could be applied, it gave the highest average results, followed in both cases by the plain acid method, then Jackson and Gillis method IV, whereas the invertase method gave the lowest average values. Considering the products in these series individually, Jackson and Gillis method II gave the highest results of all four methods in eleven out of a total of fourteen cases, and in the remaining three, the plain acid method gave the maximum figures. This is in agreement with the statement made above that the plain acid method may give any kind of result, depending on the composition of the product.

In every single case Jackson and Gillis method II gave higher figures than either the invertase or Jackson and Gillis

method IV. This shows that all the fourteen samples contained reversion products as well as amino compounds. The quantity of the reversion products, expressed as sucrose, in the refinery blackstraps varies from 0.64 to 1.32 per cent, averaging 1.12 per cent; and the quantity of amino compounds from 0.40 to 0.89 per cent, averaging 0.61 per cent. In the filtered sirups there are found 0.10 to 1.03 per cent, averaging 0.57 per cent, of reversion products, and 0.11 to 0.66 per cent, averaging 0.29 per cent, of amino compounds, all again expressed as equivalent sucrose. Expressed as asparagine or aspartic acid, the content of amino compounds in blackstraps and refinery sirups is, according to data given by Ambler (*1*) and by Browne (*4*), very much higher, in the neighborhood of 2 to 2.5 per cent.

Leaving out Jackson and Gillis method II, and comparing the results of the other three methods for all the three groups of products analyzed, it is found that the plain acid method gives the highest average results, 0.10, 0.26, and 0.15 per cent, respectively, higher than Jackson and Gillis method IV. The average figures by this last-named method again exceed those of the invertase method by 0.28, 0.51, and 0.47 per cent, respectively, owing to the differential effect of reversion products and of amino compounds.

Upon making individual comparisons, it is found that Jackson and Gillis method IV gives a higher result than the invertase method in twenty-one cases. In all of these the reversion products, expressed as sucrose, exceed the amino compounds, expressed the same way; in the remaining two cases, samples 7 and 19, the opposite is true, as actually shown in sample 7 by comparison with the result of Jackson and Gillis method II.

The plain acid method gives the highest result in nineteen cases, including all the raw sugar blackstraps, intermediate results in three, and the lowest result in one case, again proving the statement made above with regard to this method.

The invertase method gives the lowest result in all samples but three. In two of these exceptions, samples 7 and 19, this is due to the preponderance of amino compounds over the reversion products, as already explained. In the last remaining case, sample 13, the acid method happens to give the lower result, but with a difference of only 0.03 per cent, which is well within the limit of error.

The application of the results, previously obtained with artificial mixtures, to the analysis of actual cane products has thus shown that Jackson and Gillis methods II and IV, used in conjunction with the invertase method, give valuable indications with regard to the relative quantities of reversion products and of amino acids present in such products.

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A Rapid Method for Distinguishing Bleached Sulfate from Bleached Sulfite

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No stain appears to be known which clearly differentiates between bleached sulfate and bleached sulfite in pulp and paper. The following formula affords a simple method of indentification.

One gram of sodium carbonate is dissolved in 175 cc. of distilled water, and to this solution 1 gram of c. p. brazilin is added, stirring until dissolved. The solution gives sharper differences if used fresh. If retained for future use, air should be excluded. The solution may be applied directly to the sample to be identified, or if the preparation of a microscope slide is desired, the procedure is as follows:

One gram of pulp or paper is disintegrated by boiling for 10 minutes with distilled water. The fiber is screened and shaken up with 50 cc. of water. The micro-slide is prepared by placing 4 drops of the fiber suspension on the slide and allowing to dry. The slide is then plunged for an instant into the stain solution prepared as directed above. Excess stain solution is removed with hardened filter paper, a few drops of U. S. P. white paraffin oil are placed on the slide, and any excess oil is removed.

Bleached sulfite is stained a wine-red color, and bleached sulfate (Kraft) is stained a purple color by the brazilin solution.

If the analyst encounters a slide containing some fibers which appear doubtful as to identification, he should prepare a duplicate slide and test it with Lofton-Merritt stain, in order to eliminate the possibility of reporting as bleached fibers some which in reality are partially bleached. If the Lofton-Merritt stain shows a sulfate reaction, and yet with brazilin the fibers react to produce a lighter shade than the deep purple of the fully bleached sulfate, the obvious conclusion would be that these fibers are partially bleached sulfate. Similarly, if the Lofton-Merritt stain shows a sulfite reaction, and yet the fibers react with brazilin to produce a lighter shade than the vivid wine-red of the fully bleached sulfite, the conclusion would be that these fibers are partially bleached sulfite.

To emphasize the supersensitivity of this stain to all contamination, the following explanatory data are added:

Method of Disintegration. The standards of the Technical Association of the Pulp and Paper Industry have been adopted in all other microanalyses, and at the beginning of work on brazilin every effort was made to have the technic conform to those standards. This was found impossible, however, because the stain is so very sensitive. The slightest trace of acid, or addition or subtraction of alkali, makes the stain worthless, and, although the author has tried the T. A. P. P. I. method of disintegration many times for this stain, results have never been successful. An explanation is that all the sodium hydroxide is not washed out after boiling

and hence interferes with the reaction. In the case of hard sized papers, the boiling time is increased in order to get the proper disintegration.

Drying of Slide. The slide may be either dried or blotted. However, the author's reason for preferring drying is solely to eliminate one more possibility of contamination—the blotting medium.

Method of Staining. There may also be some question as to whether it is better to immerse the slide in the staining solution or to drop the solution upon the slide. Either method of staining is satisfactory. However, if the dropping method is used, sufficient stain should be dropped on the slide from a pipet to cover all fibers at once, since the most important part of the staining procedure is to remove the excess stain instantly. No mixing of the stain with the fibers is necessary. In fact it is detrimental, as this stain permeates the fibers instantly on contact.

There may also be some question as to the economy of immersing the slide, instead of dropping the stain upon the slide. For analyses which make only one or two slides necessary, only a portion of the specified amount is made up. C. P. brazilin, made by the MacAndrews & Forbes Co., 200 Fifth Ave., New York, N. Y., at 50 cents per gram, is used.

The oil immersion is not absolutely essential, but sharper differentiation can be obtained with oil than with water.

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Equipment for Laboratory Fumigations with Hydrocyanic Acid

With Controlled Temperature and Humidity

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HYDROCYANIC acid is used extensively for field fumigations of citrus trees, particularly in the control of the red scale, *Chrysomphalus aurantii*. In field work it is very difficult to duplicate exactly any given treatment, owing primarily to the lack of control over meteorological conditions. In order to pursue various research problems relating to the toxicity of hydrocyanic acid to red scale, it is of great advantage to be able to make fumigations in the laboratory under closely controlled conditions. This paper describes an assembly which has been found satisfactory for such experiments. Provision is made for the control of hydrocyanic acid concentration, relative humidity, time, and temperature of treatment.

Fumigation Chamber

Laboratory toxicity tests may be made by fumigating lemons which are moderately heavily infested with red scale. The lemons are cut with stems about 4 inches (10 cm.) long.

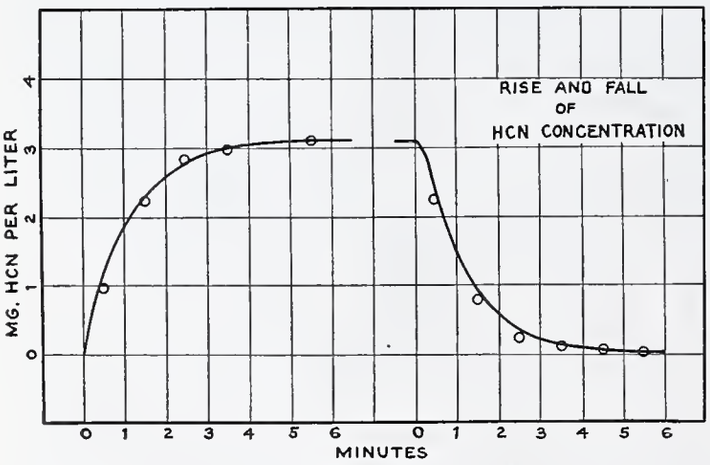

Figure 1

They may be kept in good condition for a sufficient length of time after a fumigation to provide for satisfactory mortality counts. The fumigation chamber, which will conveniently accommodate four lemons, is adapted from a glass desiccator, 200 mm. inside diameter, with ground-on cover tubulated to accommodate a rubber stopper. Inlet and outlet tubes for the air–hydrocyanic acid mixture enter through the rubber stopper, the inlet tube opening at a point near the bottom of the desiccator and the outlet tube opening near the extreme top. Tests with fumes of ammonium chloride, using a gas flow of 6 liters per minute, have shown that sufficient turbulence is produced within the desiccator to insure a uniform distribution of the hydrocyanic acid.

A support is provided within the desiccator to which the lemons are tied, and when the lemons are in place the desiccator may be covered and entirely immersed in a water thermostat. The bottom portion of the desiccator contains enough metallic lead to sink the desiccator to the bottom of the thermostat. The inlet and outlet tubes for the gas mixture are long enough to protrude above the surface of the water, and they are connected to the other units with short rubber connectors.

In the fumigation of red scale with hydrocyanic acid it is desirable, for maximum effectiveness, that the concentration be increased to its maximum value within a short period of time (*2*, *3*). Although this requirement would not seem to be so vital for the performance of comparative laboratory tests, nevertheless it has seemed desirable to obtain a comparatively rapid increase of concentration. This has been attained by using a fumigation chamber having the relatively small volume of 4 liters, and by supplying the air–hydrocyanic acid mixture at the rate of 6 liters per minute. Experiments have been made to determine the rate of increase of concentration at the start of a fumigation, and the rate of decrease of concentration at the close, at which time the fumigation chamber is usually swept out with air. The gas samples for these analyses were taken from the outlet tube leading from the top of the chamber, and thus represent a somewhat less favorable situation than at a point centrally located within the fumigation chamber. These results are represented graphically in Figure 1.

Flow Diagram and Description of Apparatus

A flow diagram of the assembly is shown in Figure 2. Air enters through the flowmeters, *A* and *B*, and is finally exhausted to the atmosphere outside the building by a motor-driven exhaust pump. The major portion of the air, about 6 liters per minute, enters through flowmeter *A* and is brought

to a desired temperature and humidity in the absence of hydrocyanic acid. A much smaller flow of air, about 200 cc. per minute, enters through flowmeter *B*. This portion picks up hydrocyanic acid in two "saturators" and is then mixed with the main current of conditioned air. The mixed gases pass through the fumigation chamber and are then exhausted to the atmosphere. The rate of flow of the mixed gases is controlled primarily by needle valve 1, but a portion of the gas flow, controlled by needle valve 2, passes through the gas analysis apparatus. This apparatus, of the flowmeter type, is similar to one described elsewhere (*1*). For the

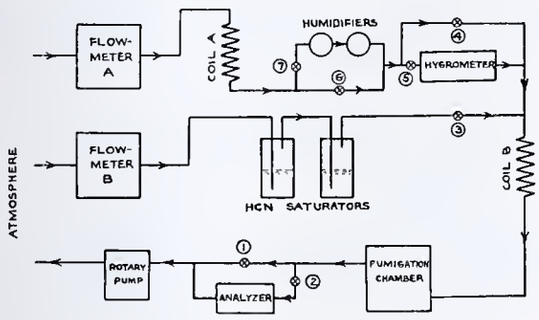

Figure 2. Flow Diagram

control of temperature, certain units are immersed in a water thermostat. The parts so immersed include the fumigation chamber, the humidifying towers, the hydrocyanic acid saturators, and two copper coils which serve to bring the gas stream to the temperature of the water bath.

The main flow of gas, entering through flowmeter *A*, is brought approximately to the temperature of the water bath by passage through a copper coil which is immersed in the bath. The humidity may be adjusted by properly setting valves 6 and 7, thus causing any desired part of the air to pass through the humidifying towers, which are simple, glass-packed columns kept moistened with water. While the humidity is being adjusted, the air current is passed through a hygrometer of the wet- and dry-bulb type, illustrated in Figure 3. After adjustment of the humidity, valve 4 is opened and valve 5 is closed, thus by-passing the air stream around the hygrometer. This avoids any increase of humidity due to evaporation from the wick of the wet bulb. The hygrometer has been designed to obtain a rapid flow of air past the wet bulb, and tests have shown that it functions in a satisfactory manner. Valves 4, 5, 6, and 7 are screw clamps on short rubber connections. Valves 1, 2, and 3 are needle valves which permit close control of the rates of flow.

The smaller current of air, entering through flowmeter *B*, is controlled by needle valve 3. In passing through two saturators in series, this air picks up sufficient hydrocyanic acid to produce the desired concentration in the final mixture. It may be noted that this current of air will be substantially saturated with water vapor at the temperature of the saturating bottles, and that the relative humidity of the final gas mixture will be influenced to some extent by the water vapor contained therein. This may be compensated for by suitably adjusting the humidity of the larger air stream which passes through the hygrometer. The combined gases flow through a second copper coil and into the fumigation chamber.

Method of Supplying Hydrocyanic Acid

Each saturator is a one-gallon bottle containing 2 liters of aqueous hydrocyanic acid. Initially the concentration of hydrocyanic acid is the same in both bottles, but as an experiment progresses the concentration in the first bottle falls below that in the second. The air is slowly bubbled through the solution and reaches approximate equilibrium with it. The concentration of hydrocyanic acid in this air will depend, therefore, upon the concentration of the solution and its temperature. The concentration of the final gas mixture will depend upon the same factors and, in addition, the fraction of the total air which passes through the saturators.

The hydrocyanic acid solution may conveniently be prepared by dissolving in water the required amount of sodium cyanide, and then acidifying with an excess of dilute sulfuric acid. An excess of sulfuric acid, because of its low volatility, will not contaminate the air–hydrocyanic acid mixture. With a solution originally containing 18 grams of sodium cyanide per liter, maintained at 23° C., the described apparatus conveniently produces final gas concentrations ranging from 0.25 to 2.00 mg. of hydrocyanic acid per liter. The range may, of course, be changed by slight alterations in the apparatus.

One of the objectives in mind when designing this apparatus was to be able to maintain a substantially constant concentration of hydrocyanic acid for a desired period of time. The question naturally arises as to the rate of decrease of concentration which may be expected due to loss of hydrocyanic acid from the saturators. It would be possible, of course, to employ some form of saturating device which would be fed by a constant stream of fresh solution. The present arrangement, however, is simple in construction and in

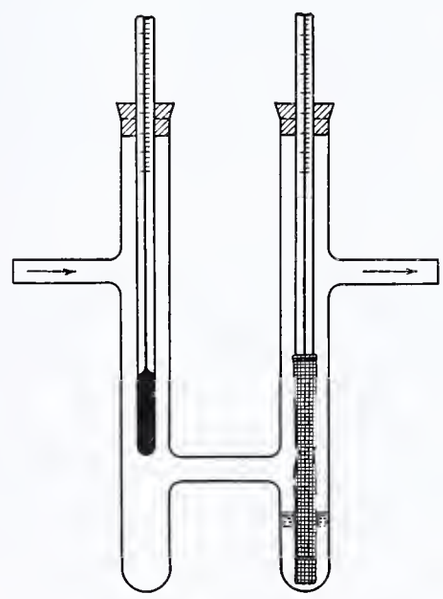

Figure 3. Hygrometer

operation, and it has been designed to minimize such concentration changes. For this purpose the following features have been incorporated:

1. A relatively large volume of hydrocyanic acid solution is used.
2. The "dilution factor" is comparatively high. That is, the air which passes through the saturating bottles is diluted many times to produce the final desired concentration. This enables the use of higher concentrations of hydrocyanic acid in the saturating bottles, and thereby reduces the percentage change of concentration therein.
3. Two saturating bottles, in series, are used. This greatly reduces the concentration change in the second bottle. If still greater constancy is desired, a third bottle may be added.

Calculations have been made to determine just what performance might be expected from the present apparatus in respect to such concentration changes. Assuming average operating conditions, it has been calculated that a continuous 5-hour run would cause a reduction in the gas concentration of less than 0.6 per cent. This in itself represents a fair degree of constancy, and it is evident that the variation during shorter

periods of time will ordinarily be negligible. Moreover, it is possible to readjust the concentration at any time by slightly varying the rate of flow through the saturating bottles.

ACKNOWLEDGMENT

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A Simplified Karns Technic for the Micro-Estimation of Iodine

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IN THE estimation of the minute quantities of iodine which normally occur in animal and vegetable matter, the step of greatest difficulty has been the destruction, without loss of iodine, of the organic matter present. Earlier workers used fusion with alkali, with or without nitrate, while in recent years combustion in a current of oxygen in a silica or Pyrex tube, ignition in a muffle at a controlled low temperature, or digestion with hydrogen peroxide and sulfuric acid has been employed with varying success in different laboratories.

Alkaline fusion is applicable only to small samples, and introduces large quantities of reagents, which in themselves constitute a danger of contamination. Low-temperature ignition in a muffle (450° C.) was proposed by Remington (*5*), and used on a large number of samples of vegetables. The authors were able to show good recoveries when dried thyroid gland was added to dried potatoes, but Reith (*8*) reported large losses when iodine compounds were added to cereal products or dried milk. Karns (*3*), on the other hand, found good recoveries of added potassium iodide, but that plant and animal tissues alone gave consistently lower values than by other methods.

Digestion with hydrogen peroxide and sulfuric acid, proposed by Pfeiffer (*7*), requires costly and fragile apparatus, and possesses objections which include the distillation of unoxidized fatty acids and other volatile substances, inability to handle large samples, and time required for the oxidation.

The silica tube furnace devised by McClendon (*4*) and adopted with various modifications by Reith, von Fellenberg (*1*), McHargue (*6*), and others, insures, with proper operation, rapid and complete oxidation in a semi-enclosed system, all evolved gases being drawn through an absorption train. The capacity of the absorption system has to be large, so that while the actual combustion of the sample may take half an hour or less for 100 grams, the subsequent evaporation and manipulation of the large volume of absorption liquid and washings will require several days. The intense heat developed in the McClendon furnace, in an atmosphere enriched with oxygen, creates conditions favorable to fixation of atmospheric nitrogen. Nitrite, thus formed, is hard to get rid of, and unless eliminated may oxidize and drive out of solution all the iodine present. Complete failures to recover any iodine by this method are annoyingly frequent. Recently Karns (*2*) has proposed ignition in oxygen in a specially constructed flask or bulb, claiming that the oxidation could be made slower and could be more easily controlled, and that hence it is possible to work with a much smaller absorption train than with the tube furnace. Karns also introduced the idea of condensing the evolved iodine by freezing, instead of absorbing it in solutions.

The method of Karns seemed to be a distinct advance, particularly for those laboratories where iodine assays must be made frequently, and the authors accordingly undertook to simplify the apparatus and manipulation. The essential part of the simplified set-up is the torch (Figure 1) which contains combined in one piece of apparatus the feed device for the sample, jets for supplying oxygen, exit tube for products of combustion, and support for the flask or combustion chamber. It is made of brass, the cup being of such size as to accommodate and provide water seal for a 500-cc. wide-mouth Erlenmeyer flask of Pyrex glass. The oxygen feed tubes are so set as to throw the jets of oxygen against the tip of the advancing candle, and are offset slightly so as to give the gaseous stream a whirling motion. For dry milk and some other substances two oxygen jets are sufficient, but for samples more difficult to burn cleanly torches with four jets have been constructed. Oxygen consumption approximates 1 to 1.5 liters per minute. The Erlenmeyer type of flask was chosen after many trials as giving the maximum efficiency with the least volume.

An essential part of the operation is the manner of feeding the sample. This is packed into Visking sausage casing[1] (0.94 inch, 2.35 cm.) to form a cartridge which fits very freely in the feed tube. The feed plate has two pins projecting from its upper surface, which engage the cartridge and cause it to rotate with the feed screw, thus enabling the oxygen jets to exert a cutting action as the cartridge advances. With this device it has not been found necessary to use carbon dioxide, but the feed tube is provided with a hole near the lower end, to permit a small amount of air to be drawn in and guard against the water seal being broken by sudden changes of pressure. The exit tube leading to the absorption train is of glass rather than metal, since the products of combustion are apt to be corrosive, and all brass surfaces exposed in the combustion chamber and water-seal cup are given a coating of nitrocellulose lacquer, it having been found that copper in the washings may interfere in the analysis.

Samples of dry milk or dried vegetable matter weighing 25 to 50 grams can be burned readily in one operation. The combustion can be interrupted to introduce new cartridges of material, or to change the flask, should it become so coated with sublimed material as to make proper observation of the operation impossible. Good vision of the tip of the burn-

[1] The Visking sausage casing may be objected to as a possible source of iodine, but we have used it continuously for several years when burning samples in the silica tube. Some of the diets employed to produce goiter in the rat contain so little iodine (15γ per kilo) that a kilogram must be burned in one sample, and any appreciable amount of iodine in the sausage casing would become evident.

ing candle is important, for if the sample is fed too fast combustion will be incomplete and tarry products formed. This is shown by the color and appearance of the flame.

With regard to the absorption train, Karns has shown that absorbing liquids can be dispensed with and gaseous iodine compounds frozen out, using solid carbon dioxide and acetone as the refrigerant. Since the flask and absorption tubes must afterward be rinsed with water containing some alkali, an efficient liquid absorption system, provided the volume of liquid and amount of alkali could be kept

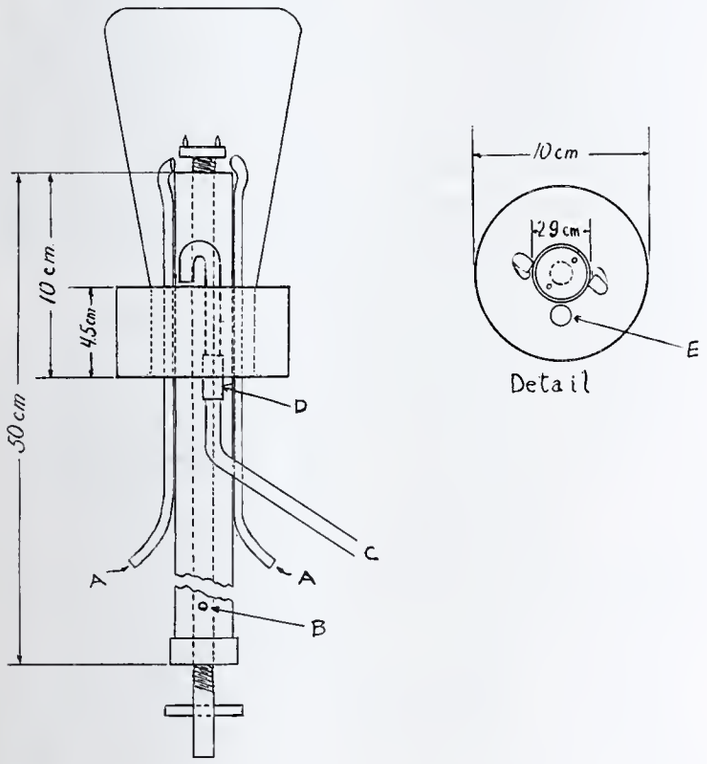

Figure 1. Essential Part of Simplified Set-Up. Detail Shows Manner in Which Oxygen Tubes Are Offset

A. Oxygen feed tubes, 5 mm. outside diameter. Standard copper tubing
B. Air vent, 3 mm. diameter (important)
C. Glass outlet tube, 7 mm. outside diameter, connected with Milligan absorbers
D. Rubber tubing gasket for outlet tubes
E. Hole for outlet tube, 9 mm.

small, should possess no disadvantages over the refrigeration method, and would be simpler in operation. The electrical precipitator, introduced first by McClendon to remove solid particles from the gas stream, has proved so inconvenient in operation and of so little value in the analysis that it was discarded by McClendon as well as by the authors several years ago. With the slow burning possible in the Karns type of apparatus and efficient wash bottles, no more trouble is experienced from dust, most of it being deposited in the flask and the balance in the absorption apparatus. The authors use only two Friedrich's or Milligan wash bottles in series, the two bottles being identical as to type and giving equally satisfactory results, but the Friedrich's bottle requiring much less liquid. Rhodes and Rakestraw (*9*) report this type most efficient of seven kinds tested. Two pellets of sodium hydroxide are added to the water in the first bottle, and one in the second. Practically all the iodine will be found in the washings of the flask and the contents of the first absorber, as noted by Karns (*2*). The relative distribution will depend on the amount of iodine in the sample and rate of burning. For example, burning 25 grams of a sample of milk powder which contained the enormous amount of 2000 γ of iodine, 9.9 per cent was found in the flask, 87.2 per cent in the first Milligan wash bottle, and 2.2 per cent in the second. With Friedrich's bottles the partition was 6.1, 83.3, and 10.2 per cent, respectively, the difference being due to the larger orifice and more rapid gas flow in the latter case. Ordinarily the second wash bottle serves only as a trap to collect splashings from the first.

After the combustion, the water from the cup is used to rinse the flask, combined with the solutions from the absorbers, and the whole apparatus is rinsed with a minimal amount of water. After testing to insure alkalinity, the combined solutions are concentrated to small volume in a beaker, centrifuged free from insoluble matter, and evaporated to dryness in a platinum dish. An additional pellet of sodium hydroxide is added to the dish and the contents just fused, holding the dish with tongs and keeping it moving over the flame. This quick fusion has been found necessary to destroy any organic dust particles that may have found their way into the solution.

If the iodine is to be determined colorimetrically, extraction with alcohol can frequently be dispensed with, the contents of the dish being dissolved in a small volume of water, a pinch of sodium azide added to decompose nitrites, followed by a little sodium sulfite to reduce iodate, this in turn by phosphoric acid to acidity, then boiling to expel sulfur dioxide transferring to the small separatory funnel. A minute crystal of sodium nitrite will now liberate the iodine, which is taken up with 1 cc. of carbon tetrachloride and compared with a standard in a microcolorimeter.

If iodine is to be estimated by titration, the reduced residue in the platinum dish should be extracted several times with alcohol, the alcohol removed by evaporation, iodide oxidized by bromine, and the balance of the determination carried out in the usual way. In this laboratory results by titration are invariably somewhat higher than by colorimetry, and since the possibility of the presence of traces of reducible substances other than iodate cannot be rigorously excluded, the colorimetric method is preferred.

The results given in the following table indicate that recoveries are quite as good with this apparatus as with more complicated trains.

Method	Sample Dry Milk Taken	Iodine in Sample	Iodine Added	Total Iodine Present	Iodine Recovered	Recovery
	Grams	γ	γ	γ	γ	%
Silica-tube furnace	50	27.7	...	...	...	...
	50	26.8	...	...	...	...
	50	27.8	...	...	...	...
Flask	25	14.7	...	...	...	...
	25	15.1	...	...	...	...
	25	14.5	...	...	...	...
Flask; iodine added as NaI	25	14.9	14.0	28.9	27.1	93.7
	25	14.9	14.0	28.9	30.0	103.8
	25	14.9	25.0	39.9	38.5	96.5
Flask; iodine added as thyroid powder	25	14.9	25.0	39.9	40.1	100.5
	25	14.9	25.0	39.9	38.0	95.2
	25	14.9	100.0	114.9	116.0	100.9

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Determination of Zirconium in Steels

Selenious Acid Method

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Zirconium can be satisfactorily determined in steels by precipitation from dilute hydrochloric acid solution with selenious acid in the presence of hydrogen peroxide, and ignition of the precipitate to zirconium dioxide. The method has been found applicable to steels containing elements ordinarily present in zirconium steels. The presence of tungsten may cause contamination of the final selenite precipitate, and requires an additional step in the procedure.

Titanium can be determined—colorimetrically for small amounts, with cupferron for larger amounts—in the filtrate from the precipitation of zirconium selenite, but the large volume of solution and the presence of selenious acid and hydrogen peroxide, as well as iron and possibly vanadium, all of which must be removed, make it more feasible to determine titanium on a separate sample, or on an aliquot portion of the solution previous to the zirconium precipitation.

THE determination of zirconium by precipitation with selenious acid was first suggested by Smith and James (*6*), and the method has been applied to the determination of zirconium in minerals by Simpson and Schumb (*5*), but the nature and amounts of constituents present in steel are so different from those in minerals that it seemed advisable to determine the applicability of the selenite method to the determination of zirconium in steels.

Solutions Used. In most of the following analyses, 3-gram samples of a plain carbon steel were used, and to each solution were added definite amounts of zirconium in the form of a zirconyl chloride solution, as well as definite amounts of salts of other elements, as indicated. In this way, solutions of artificial steels were prepared containing any desired amounts of constituents.

Elimination of Interfering Constituents. In devising a tentative method for the determination of zirconium in steel by the selenite method, it seemed advisable to follow as closely as possible the selenite method as applied to ores, making only those changes which the entirely different nature of the sample obviously demands. A method for zirconium in steel should allow for the possible presence not only of those constituents present in a plain carbon steel, but also of aluminum, titanium, chromium, tungsten, vanadium, molybdenum, cobalt, nickel, copper, uranium, and in certain rare cases possibly of tin, arsenic, columbium, and tantalum. The possible effects of these constituents should therefore be considered before modifications of the selenite method are proposed in order to fit the analysis of steels.

Iron. In the regular selenite method for minerals, it was shown that, although iron is precipitated by selenious acid from neutral solution, it is not so precipitated from solutions containing mineral acid, and zirconium can therefore be precipitated nearly free from iron by a single precipitation and entirely so by a double precipitation. In steel, however, the percentage of iron is so great that it would seem advisable to remove at least the greater part of it early in the analysis. Such removal can be most readily effected by shaking the hydrochloric acid solution with ether.

Molybdenum. According to Blair (*2*), molybdenum in the hexavalent condition is 80 to 90 per cent removed by a single extraction with ether from hydrochloric acid solution, and is 100 per cent removed if ferric chloride is also present. The ether extraction used for the partial removal of iron should therefore suffice for the removal of all the molybdenum in the solution.

Carbon, Silicon, and Tungsten. These constituents are removed by filtration subsequent to the usual procedure of evaporation of the solution and dehydration of the residue.

Phosphorus. Phosphorus would cause precipitation of at least part of the zirconium as zirconium phosphate and remain in the silica residue, but the zirconium would be recovered free from phosphate by a sodium carbonate fusion of the residue and subsequent solution of the residue in acid.

Titanium, Aluminum, Chromium, Vanadium, Cobalt, Nickel, Copper, and Uranium. The precipitation of zirconium selenite from acid solution containing hydrogen peroxide has been shown in the preceding work to cause nearly complete separation of zirconium from these constituents by a single precipitation, and a complete separation by means of a double precipitation.

Thorium. Thorium, which caused interference with the selenite method as applied to ores and required additional steps in the procedure for its complete removal, is not present in steels and need not be considered.

Effect of Ether and Acidity. In applying the proposed method given below to the analysis of solutions of steels containing added amounts of zirconyl chloride, it was found necessary to use alcohol-free ether in the extraction of iron, since ordinary ether has a marked solvent action on zirconyl chloride. Furthermore, with small amounts of zirconium it was found that the acid normality of the solution from which zirconium selenite is precipitated should be less than that used in the case of ores and should not be much greater than 0.3 N in hydrochloric acid.

Proposed Method for Determination of Zirconium in Steel

Dissolve 3 grams of steel in 40 cc. of concentrated hydrochloric acid. When solution is complete or nearly so, add sufficient concentrated nitric acid to oxidize the iron. Evaporate to dryness on the steam plate, moisten the residue with 6 N hydrochloric acid, evaporate to dryness, heat at 105° C. for 30 minutes, and treat with 30 cc. of 6 N hydrochloric acid and 50 cc. of hot water. After all soluble salts have dissolved, filter and wash the residue with dilute hydrochloric acid and finally with hot water. Treat the filtrate and residue separately[1] as follows:

Filtrate. Evaporate the filtrate nearly to dryness, add 40 cc. of 6 N hydrochloric acid, and extract twice with 40 cc. of alcohol-free ether. Evaporate the aqueous solution to complete dryness, dissolve in 12 cc. of 12 N hydrochloric acid, dilute to 400 cc., heat nearly to boiling, add 15 cc. of

[1] In the presence of much phosphate, most of the zirconium will be found in the residue; with little or no phosphate, most of the zirconium will be found in the filtrate.

3 per cent hydrogen peroxide and 20 cc. of a 10 per cent solution of selenious acid, and allow to stand until any precipitate has coagulated. Filter, wash with hot water, and unite with the corresponding precipitate obtained from the residue below.

RESIDUE. Ignite the siliceous residue in platinum. Treat with sufficient hydrofluoric acid (and two drops of concentrated sulfuric acid) to volatilize the silica. Evaporate to dryness and fuse with sodium carbonate. Extract with hot water, filter, wash with dilute sodium carbonate solution and then with hot water. Ignite the residue and fuse with potassium pyrosulfate. Dissolve in 100 cc. of hot water containing a few drops of sulfuric acid, make ammoniacal, filter, wash with hot water, and dissolve the precipitate in 25 cc. of 6 *N* hydrochloric acid. Dilute to 400 cc., heat nearly to boiling, add 15 cc. of 3 per cent hydrogen peroxide and 20 cc. of 10 per cent selenious acid solution, and allow to stand until the precipitate has coagulated. Filter, wash with hot water, and unite with the corresponding precipitate obtained from the main filtrate. (The two solutions should not be united prior to the precipitation of zirconium selenite, since the solution from the treatment of the residue may contain phosphate and thus cause zirconium phosphate to precipitate.) If the zirconium precipitate is large, dissolve it in 25 cc. of hot 6 *N* hydrochloric acid,[2] dilute to 400 cc., add 15 cc. of hydrogen peroxide, and reprecipitate with selenious acid. Ignite the precipitate and weigh as zirconium dioxide.

RESULTS BY PROPOSED METHOD

In the analyses made by the proposed method, 3 grams of a plain carbon steel were dissolved and to the solution were added measured amounts of zirconyl chloride solution corresponding to (*a*) 0.15 per cent, (*b*) 0.38 per cent, and (*c*) 1.92 per cent of zirconium in the original steel. In addition, 20 mg. each of the other metals in the form of solutions of their salts were added. The results obtained are shown in Table I.

TABLE I. ANALYSIS OF PLAIN CARBON STEEL SAMPLES

(Sample, 3 grams plain carbon steel)

CONSTITUENTS ADDED (20 MG. OF EACH METAL)	ZR FOUND WHEN ZR PRESENT = 0.0046 GRAM, 0.15%		ZR FOUND WHEN ZR PRESENT = 0.0115 GRAM, 0.38%		ZR FOUND WHEN ZR PRESENT = 0.0575 GRAM, 1.92%	
	Gram	%	*Gram*	%	*Gram*	%
None	0.0046	0.15	0.0115	0.38	0.0577	1.92
Ti^{++++}, Al^{+++}	0.0047	0.16	0.0108	0.36	0.0572	1.91
	0.0048	0.16	0.0118	0.39	0.0582	1.94
Ti^{++++}, Al^{+++}, UO_2^{++}, VO_3^-	0.0048	0.16				
	0.0042	0.14				
Ti^{++++}, Al^{+++}, Cr^{+++}, VO_3^-	0.0042	0.14	0.0109	0.36	0.0575	1.92
	0.0047	0.16			0.0595	1.98
	0.0046[a]	0.15			0.0598	1.99
Ti^{++++}, Al^{+++}, Cr^{+++}, VO_3^-, UO_2^{++}, Co^{++}, Cu^{++}, Ni^{++}	0.0048	0.16	0.0118	0.39	0.0581	1.94
Ti^{++++}, Al^{+++}, UO_2^{++}, VO_3^-, WO_4^{--}, MoO_4^{--}	0.0062	0.21	0.0132	0.44		
WO_4^{--}, MoO_4^{--}	0.0047	0.16	0.0115	0.38	0.0738	2.46
	0.0047	0.16	0.0141	0.47	0.0751	2.50
	0.0053	0.18	0.0146	0.49	0.0747	2.49
WO_4^{--}	0.0047	0.16			0.0763	2.54
					0.0665	2.22
MoO_4^{--}					0.0572	1.91

[a] Bureau of Standards cast iron No. 74 (0.464 per cent P).

It is seen that the proposed method for zirconium gives satisfactory results except in cases where tungsten is present. The presence of that element tends to give variable values which are especially high in the case of mixtures containing considerable amounts of zirconium, and in such cases the final precipitate on examination showed the presence of large amounts of tungsten but no appreciable amounts of other contaminants. It would seem, therefore, that the usual method of removing tungsten with silica by evaporation to dryness is not quantitative when much zirconium is present, and the unremoved tungsten is brought down by the subsequent selenite precipitate.

Since no method was found for satisfactorily breaking up what are undoubtedly one or more complex tungsten-zirconium compounds, it seemed most feasible to correct for the tungsten brought down by the final zirconium selenite precipitate. To do this, the ignited precipitate was fused with sodium carbonate, leached with hot water, filtered, washed with hot water, and the residue ignited to zirconium dioxide, the tungsten being removed in the filtrate as sodium tungstate. Table II shows the results of analyses of samples containing tungsten by the proposed selenite method with this additional step introduced.

TABLE II. ANALYSES OF SAMPLES CONTAINING TUNGSTEN

CONSTITUENTS ADDED (20 MG. OF EACH METAL)	ZR FOUND WHEN ZR PRESENT = 0.0046 GRAM, 0.15%		ZR FOUND WHEN ZR PRESENT = 0.0115 GRAM, 0.38%		ZR FOUND WHEN ZR PRESENT = 0.0575 GRAM, 1.92%	
	Gram	%	*Gram*	%	*Gram*	%
Ti^{++++}, WO_4^{--}	0.0046	0.15	0.0113	0.38	0.0580	1.93
					0.0572	1.91
Ti^{++++}, WO_4^{--}, MoO_4^{--}	0.0047	0.16	0.0112	0.37		
Ti^{++++}, WO_4^{--}, MoO_4^{--}, VO_3^-	0.0045	0.15	0.0113	0.38		
Ti^{++++}, WO_4^{--}, MoO_4^{--}, VO_3^-, Al^{++++}, UO_2^{++}	0.0047	0.16	0.0113	0.38		

DETERMINATION OF TITANIUM

As has been pointed out by Lundell and Knowles (*4*), it is advantageous in a sample of zirconium alloy to determine the percentage of titanium and zirconium in a single sample of material, although few methods for zirconium in steel make provision for such determination of titanium. In the case of the selenite method for zirconium, any titanium is in the filtrate from the zirconium precipitate, and the solution also contains iron, hydrogen peroxide, a large amount of excess selenious acid, and any vanadium, chromium, and other acid-soluble metals that may have been present in the original alloy, so that a quick isolation or determination of titanium in this solution is a matter of some difficulty. Several possible methods of determining titanium were considered, as follows:

Titanium precipitates as selenite from neutral solution with selenious acid in the absence of hydrogen peroxide, but it was found that the precipitation is not quantitative in the presence of even the small amount of free acid necessary to prevent the precipitation of iron.

Brown and Madden (*3*) have shown that titanium can be quantitatively precipitated as phosphate from the filtrate of a zirconium phosphate precipitation after the removal of any hydrogen peroxide by boiling. Unfortunately, when this method is applied to samples containing very small amounts of titanium such as would likely be present in a zirconium steel, the titanium is very slow in precipitating and is sometimes not formed after several days.

Recently, Beans and Mossman (*1*) have shown the possibility of precipitating titanium as titanium iodate from strong nitric acid solution, but the amounts of iron and vanadium present in the zirconium filtrate in the case of steels would have to be removed previously. This would likewise be true of the cupferron method.

The colorimetric determination of titanium with hydrogen peroxide is especially convenient with small amounts of titanium, but to apply this to the zirconium selenite filtrate necessitates the evaporation of a large volume of solution

[2] Occasionally with larger amounts of zirconium the precipitate does not dissolve completely in the acid, but leaves a small white residue which usually does not yield even to concentrated acid. This residue ignites to zirconium dioxide and is probably normal zirconium selenite, which, in contrast to the basic selenite, is insoluble in acid. It should therefore be allowed to remain in suspension and be included with the second precipitate of selenite.

nearly to dryness. In doing so, it was found that free selenium tends to separate out in a colloidal form difficult to filter, and also tends to give a color to the solution. In addition, the iron and vanadium present must be eliminated or corrected for. A few colorimetric determinations of titanium were attempted in various zirconium selenite filtrates, using 50-cc. Nessler tubes for comparison with standards. With 4.0 mg. of titanium originally present, the estimated amount of titanium in three determinations was between 3.5 and 5.0 mg., but the time spent in the determinations makes the method impracticable for ordinary use. It would be preferable to determine the titanium independently on an aliquot portion of the solution prior to the precipitation of zirconium selenite.

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Determination of Small Amounts of Invert Sugar in the Presence of Sucrose

Revised Procedures

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The analysis of beet sugar factory products involves the determination of small amounts of invert sugar in the presence of relatively large amounts of sucrose. With the exception of the Herzfeld method, which is directly applicable only to the analysis of raw sugar and to which there are certain objections, present methods are not well adapted to the determination of invert sugar in beet sugar factory products, including molasses.

Preliminary investigations covered various details and in particular confirmed the necessity of improvement in the usual methods of preparing Fehling solutions. A procedure applicable to all beet sugar factory products is described, and two methods of carrying out the copper reductions are recommended. Advantages and disadvantages of the two methods are discussed, and complete tables for the use of both methods are given.

The analysis of beet sugar factory products involves the determination of small amounts of invert sugar in the presence of relatively large amounts of sucrose. Present methods do not have tables that are suitably worked out for ratios of sucrose and invert sugar in the variety of products encountered, and the reduction procedure is open to various objections. The Herzfeld method (*5*, *9*), which still has international usage, is applicable only to raw sugar and cannot be used for molasses without serious error. Analysts also complain of the difficulty of securing check results by the Herzfeld method, which is attributed by Pick (*12*) to local overheating of the solution caused by the application of intense heat.

In order to make the methods applicable to all beet sugar factory products of widely varying concentration and purity, the following simple procedure is employed: The calculated amount of the test sample is weighed out which will yield exactly a desired and definite amount of dry substance (5 or 2.5 grams) in the 50 ml. of solution used to reduce the Fehling solution. This calculation is abridged by the use of tables, and, in place of true dry substance, refractometer or Brix values may be used if desired. By constructing copper tables, in which the reducing effect of various amounts of sucrose (5, 2.5, and 1.5 grams) is taken into account, the invert value may be obtained from knowledge of the approximate purity of the product under examination. The invert values in the copper tables are expressed as percentages on dry substance, which is often the basis desired in recording data or comparing the amount of invert sugar in a series of different products.

The Quisumbing and Thomas (*13*) investigation deserves more attention than it has received on the part of sugar chemists, although their method has been adopted by the Association of Official Agricultural Chemists (*1*) for the determination of reducing sugars in plants. The Quisumbing and Thomas tables, however, are not sufficiently comprehensive to cover the ratios of sucrose and invert sugar usually encountered in beet products. These authors investigated many features, devised a new heating procedure for the reduction, and were the first to insist on the preparation of Fehling solutions by a method which insures exact proportions. Preliminary to adapting the Quisumbing and Thomas method to the purpose in question, the influence of some details of procedure was investigated.

Investigations

One thing which had to be decided was the amount of dry substance which should be used for the determination. It was found difficult to filter and wash the precipitate from a molasses solution containing 10 grams of dry substance (in 50 ml.), even when the amount of invert sugar present was low. A test solution containing 5 grams of dry substance gave sufficient material for accurate results, was easy to handle, and yielded a precipitate of good color. Good results were also obtained with 2.5 grams of dry substance, but the accidental error increases with decreasing concentration. The authors therefore recommend the use ordinarily of 5 grams of dry substance, and of 2.5 grams when the percentage of invert sugar is fairly high—i. e., above 1.5 per cent. Some typical results obtained with different amounts of dry substance are shown in Table I. The percentage of invert sugar found tends to increase slightly with decreasing con-

centration of the test solution. The lower results at the higher concentration are evidently due to the depressing action of the greater concentration of impurities. For this reason it is desirable to avoid high concentrations in the analysis of impure products. A question which cannot yet be definitely answered is the absolute accuracy within small limits of the values found in the analysis of an impure product like molasses.

It is unnecessary to reopen the question of lead clarification, because sugar chemists are agreed that, except possibly for products of high purity, the solution should first be clarified with neutral lead acetate and the excess of lead should be removed by a suitable reagent.

Table I. Invert Sugar Found in Molasses

	Invert Sugar in: 10 grams dry substance	5 grams dry substance	2.5 grams dry substance
	%	%	%
Sample 1	..	0.60	0.71
	0.60	0.59	0.66
	0.65	0.65	0.59
	0.62	0.67	0.62
	0.60	0.60	0.57
	Av. 0.61	0.62	0.63
Sample 2	1.19	..	1.21
	1.13	1.22	1.26
	1.18	1.16	1.28
	1.17	1.21	1.26
	Av. 1.16	1.20	1.25

In this procedure, the use of 10 ml. of neutral lead acetate solution (55° Brix) was found to be necessary for the clarification of 22 grams of molasses dry substance. The use of only 5 ml. gave incomplete clarification, as evidenced by darker solutions and high values for invert sugar, as shown in Table II. In these tests a molasses solution containing 5 grams of dry substance in 50 ml. of test solution was clarified with various amounts of neutral lead acetate and deleaded with 10 ml. of 5 per cent solution of ammonium dihydrogen phosphate and sodium oxalate.

Table II. Invert Sugar Found in Molasses

	Invert Sugar, Using: 5 ml. lead acetate	10 ml. lead acetate	15 ml. lead acetate
	%	%	%
	0.62	0.55	0.58
	0.66	0.61	0.59
	0.64	0.60	0.57
	0.95	0.84	0.88
Av. of 4 samples	0.718	0.650	0.655
	0.57	0.42	
	0.54	0.43	
Av. of 6 samples	0.66	0.58	

Solutions of neutral lead acetate prepared from c. p. chemicals were found to have a pH value of about 6.2. No difference in results was found between lead acetate of 6.0 and 7.0 pH, respectively. (See Table III.) It therefore seems unnecessary to readjust the pH of this solution.

Table III. Invert Sugar Found in Molasses Clarified with Neutral Lead Acetate

	Invert Sugar, Using Lead Acetate of: 6.0 pH	7.0 pH
	%	%
Sample 1	0.40	0.39
	0.39	0.40
	0.38	0.38
Sample 2	0.40	0.41
	0.38	0.40
	0.39	0.39
Sample 3	0.56	0.56
	0.55	0.55
	0.55	0.55
	Av. 0.444	0.448

For a deleading agent a solution containing 5 per cent each of sodium oxalate and ammonium dihydrogen phosphate has been adopted, similar to the oxalate–phosphate mixture recommended by Cook and McAllep (*8*). The use of sodium oxalate alone is unsatisfactory for beet products. The phosphate is a good precipitant for the lead, and the use of the oxalate insures the removal of calcium. Ten milliliters of the solution are sufficient for deleading 100 ml. of molasses solution when 5 to 15 ml. of lead solution have been used for clarification. Table IV shows that a considerable excess of the deleading reagent does not affect the amount of copper reduced within the limit of experimental error. On the other hand, the amount of copper reduced is seriously lowered if the excess of lead is not removed. The data in these two respects are in agreement with those of Cook and McAllep (*7*) on cane molasses.

Table IV. Effect of Reagents on Copper Reduced from Fehling Solution

Reagent	Copper Reduced: 0 ml. reagent	1 ml. reagent	2 ml. reagent	5 ml. reagent	10 ml. reagent
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
Neutral lead acetate	50.0	48.6	44.4	35.7	30.6
Oxalate-phosphate	50.0	50.5	51.0	50.4	51.8

Considerable work was done with the use of a more dilute Fehling solution, with the idea that the influence of sucrose is proportional to the amount of copper present, and that, therefore, as a great deal of the copper would be rapidly reduced by the invert sugar present, the amount left to react with the sucrose would be smaller. This procedure was tried with both the Quisumbing and Thomas and the Herzfeld methods. The idea was given up on account of the fact that both methods yielded a fine, muddy brown precipitate of a very unsatisfactory character.

The use of Fehling solutions prepared in inexact proportions or from reagents of doubtful purity is a prolific source of error in all invert sugar methods. The solutions are also subject to deterioration on long standing and should be well protected from contamination. Quisumbing and Thomas (*14*) have prescribed a definite procedure for the preparation of Fehling solutions which should eliminate any uncertainty as to their exact composition, particularly with regard to the purity and exact concentration of the sodium hydroxide in the alkaline tartrate solution. They have also modified the concentrations of these solutions on the basis of their work. The Quisumbing and Thomas modifications of Fehling solution have been employed in the methods described in this paper.

Erratic results obtained with some Fehling solutions are exemplified in Table V. In the first series the old solution B was plainly at fault. Solution 1 was carefully prepared from c. p. chemicals. The average amount of copper obtained with this solution, 19.3 mg., is in good agreement with the value of 18.0 mg. in Table IX for zero invert in the presence of 3 grams of sucrose. Solution 2 gave low results, the cause of which was not determined. Solution 3 gave high results caused by impure Rochelle salt. Solution 4 gave high and erratic results, which were found to be due to the presence of suspended copper in the bottom of the bottle of copper sulfate solution.

Table V. Variation in Amount of Copper Reduced from Fehling Solution Due to Impurities in Reagents

(Fehling solution with 3 grams sugar)

New Solutions A and B	Old Solution A New Solution B	New Solution A Old Solution B	Old Solutions A and B
Mg.	*Mg.*	*Mg.*	*Mg.*
19.5	18.7	30.3	30.6
18.8	18.5	30.3	30.0
19.5	19.0	30.3	30.3
Av. 19.3	18.7	30.3	30.3

Solution 1	Solution 2	Solution 3	Solution 4
Mg.	*Mg.*	*Mg.*	*Mg.*
19.5	13.0	25.0	30.4
18.8	13.0	25.4	23.6
19.5	13.0	25.0	28.2
Av. 19.3	13.0	25.1	27.4

The statement is made by Quisumbing and Thomas (*13*) that after 30 minutes' heating at 80° C. the reducing action of glucose on Fehling solution is practically completed. This caused the authors to do work with sucrose alone, invert sugar alone, and mixtures of invert sugar and sucrose to

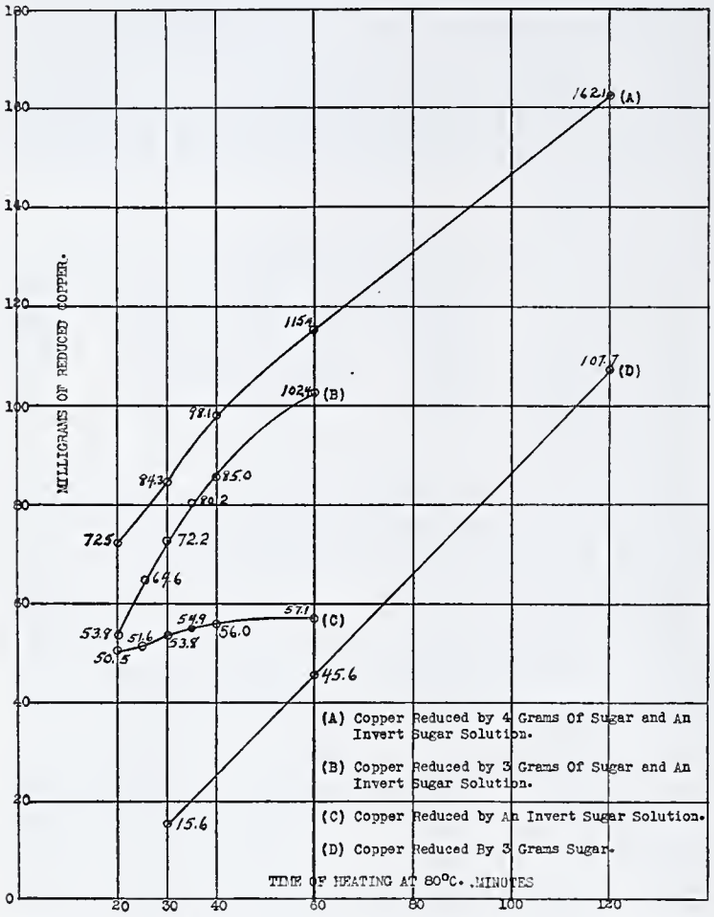

FIGURE 1. AMOUNT OF COPPER REDUCED FROM FEHLING SOLUTION BY SUCROSE AND INVERT SUGAR FOR VARIOUS HEATING PERIODS

determine their rate of reduction of Fehling solution at 80° C. The results are shown in Figure 1. Curve *C* indicates that the rate of reduction of invert sugar is slow for the period of 20 to 60 minutes. The reducing action of 3 grams of sucrose (Curve *D*) is rapid and continues at a uniform rate for 2 hours. Results for a longer time were not obtained. A mixture of invert sugar and sucrose also showed a rapid rate of reduction (Curves *A* and *B*).

Figure 2 shows that the amount of copper reduced by 3 grams of sucrose during a period of 30 minutes is considerably influenced by the temperature, the rate of reduction increasing with increasing temperature.

In the development of the method a period of 30 minutes' heating at 80° C. was employed, as recommended by Quisumbing and Thomas. These authors attempted to eliminate the reducing effect of sucrose by working at a low concentration (less than 400 mg. of sucrose). This procedure is objectionable for the purpose in question because experimental error is so much magnified at such low concentrations. Although in the adaptation of the Quisumbing and Thomas method the blank correction for sucrose is considerable, the method has many advantages.

A well-prepared asbestos mat in a Gooch crucible is the best filtering medium. The use of paper is unsatisfactory because of slow filtration and the fact that copper tends to pass through the filter. The Jena glass filter No. 1-G 4 was found to retain all the copper but required more time than the asbestos filter. Weighing the copper directly as CuO, Cu_2O, or Cu is unsatisfactory, not only because of the danger of contamination with impurities, and doubtfulness of the composition of the precipitate in the first case, but because it is exceedingly difficult to prepare asbestos mats which will not lose weight as the result of the action of hot Fehling solution. The subsequent use of acid to reclaim the asbestos tends to reactivate its solubility in alkali. New asbestos requires prolonged treatment with acid and alkali. Asbestos mats tested under such blank conditions will at times exhibit an important and disturbing loss in weight. Considerable time is required to prepare and test out an asbestos mat for a gravimetric method, and even then one cannot be absolutely certain of its subsequent behavior. Methods of titrating directly in the solution without filtering out the reduced copper can hardly be recommended, at least when the determination is made on impure products.

For the determination of the reduced copper the authors decidedly prefer the Low volumetric thiosulfate method (*3*, *10*), from the standpoints of both accuracy and convenience. The electrolytic method if properly conducted (*10*) is probably equally accurate, but electrolytic apparatus is not commonly available in sugar laboratories. These two methods are certainly in most favor among metallurgical chemists who demand a high order of accuracy and whose opinion should be given some weight. In the thiosulfate method the introduction of a layer of glass beads is advantageous in facilitating the two evaporations to expel the red fumes and the excess of bromine.

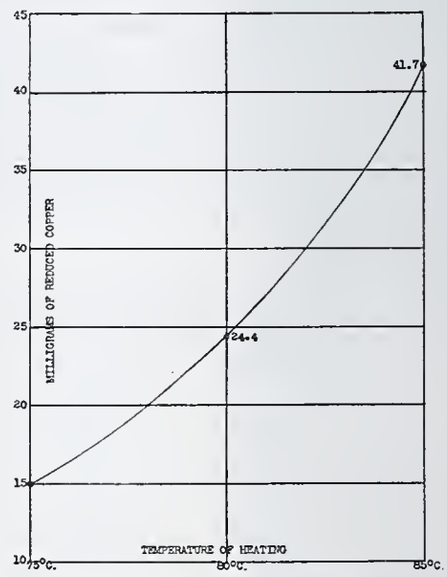

FIGURE 2. EFFECT OF TEMPERATURE ON AMOUNT OF COPPER REDUCED FROM FEHLING SOLUTION BY 30-MINUTE HEATING METHOD

The necessity of frequent preparation of the starch indicator can be avoided by the use of the de Koninck starch solution (*11*), which is described below under "Reagents."

QUISUMBING AND THOMAS METHOD

Quisumbing and Thomas carried out the reduction by immersing a beaker covered with a watch glass in a water bath. A beaker is an extremely inconvenient vessel to use in this manner and does not permit the surface of the solution to be well protected from the air during the heating period. A slight modification has therefore been made, employing a 250-ml. Pyrex Erlenmeyer flask, covered with a small watch glass, which can conveniently be clamped in place and be well submerged in the bath.

With the standard conditions selected and the details of procedure decided, points for a series of curves as shown in Figure 3 were determined and from these curves Tables VIII,

IX, and X were calculated. The relationship, within the concentrations covered, is perfectly linear and the copper values can be expressed by a straight-line formula. The points in the curves were carefully determined, each one being an average of a number of determinations made on several independently prepared solutions. The invert sugar solutions used were prepared from sucrose of high purity by inverting with hydrochloric acid for 24 hours at room temperature (*2*, *4*).

To compare the copper values with those of Quisumbing and Thomas, values in the presence of 2 grams of sucrose have been calculated by interpolation between the determined values for 1.5 and 3 grams, respectively, to compare with the Quisumbing and Thomas values in the presence of 2 grams of sucrose, the highest amount used by them. The authors' copper value for zero invert sugar in the presence of 2 grams of sucrose thus obtained is 16.0 mg., which is considerably higher than the value of 9.3 mg. in Quisumbing and Thomas' Table VIII (*13*). There is, however, a peculiar relationship in this table. If the Quisumbing and Thomas copper values for various amounts of invert sugar in the presence of 2 grams of sucrose are plotted, they form practically a straight line for all points except that representing zero invert sugar, where there is a sharp break in the curve between 10 and 0 mg. of invert sugar. This deviation does not appear consistent and is not upheld by results of the authors. The Quisumbing and Thomas copper value for zero invert sugar obtained by linear extrapolation of the straight line representing their other values is about 20 mg., which is in fair agreement with the authors' value of 16.0 mg. for the same conditions.

The highest amount of invert sugar employed in this work was 80 mg., which yielded 162.2 mg. copper in the presence of 1.5 grams of sucrose (value for 3.20 per cent invert sugar on dry substance in Table X), and 167.6 mg. copper in the presence of 3 grams of sucrose (value for 1.60 per cent invert sugar on dry substance in Table IX). By interpolation the authors' copper value for 80 mg. of invert sugar in the presence of 2 grams of sucrose would be 164.0 mg., as compared with the Quisumbing and Thomas value of 170.9 for the same conditions.

When it is considered that the manipulation has been slightly modified, the differences indicated do not appear serious, provided that the comparison for zero invert sugar is made with the Quisumbing and Thomas extrapolated value.

The amount of copper reduced by sucrose alone in this method is large—viz., 18.0 mg. for 3 grams of sucrose and 25.0 mg. for 5 grams. This is in the nature of a correction for a blank determination, and it is objectionable on general principles to use a method in which the blank correction is so great.

Close temperature control is necessary in this method. A difference of even one degree in the average temperature will, according to Figure 2, cause a variation of 2 to 3 mg. in the amount of copper reduced. While the use of a thermostatically controlled, agitated water bath would therefore seem most desirable, all the authors' work has been done with the use of an ordinary water bath, heated by steam introduced through a perforated coil and controlled manually by a 0.25-inch needle valve. This arrangement permits of sufficiently close temperature control for the order of accuracy of such a method.

In spite of these disadvantages the Quisumbing and Thomas method gives results that can be closely duplicated. Examples of such parallel tests will be found in Tables I, III, and V. Other advantages of the method are (*a*) the amount of solution to filter (100 ml.) is small, (*b*) a granular red precipitate is obtained which has settled to the bottom of the flask at the end of the heating period and therefore permits rapid filtration and washing by decantation, (*c*) the time and temperature of heating are definite, and (*d*) on account of the physical properties and settling of the precipitate, products containing relatively high percentages of invert sugar can be easily handled.

Two-Minute Heating Method

The basic idea of this method was suggested by an observation of Bruhns (*6*), who states that the reducing power of invert sugar is practically exhausted when the mixture of sugar and Fehling solution begins to boil, and that sucrose

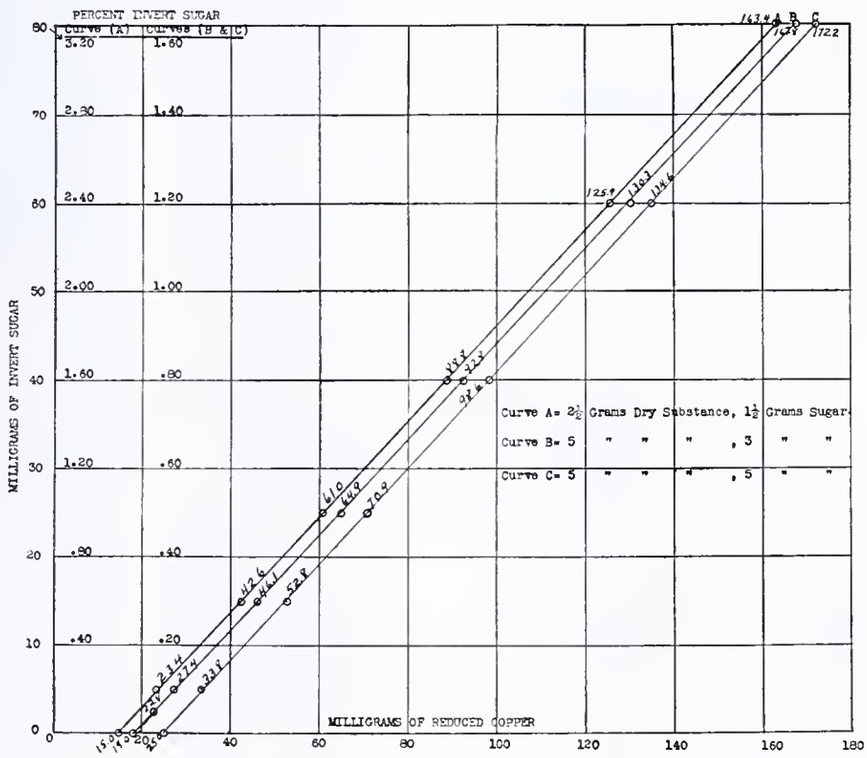

Figure 3. Percentage of Invert Sugar Calculated from Amount of Reduced Copper (Quisumbing and Thomas Procedure)

causes only slight reduction when the solution is heated rapidly to the boiling point. It therefore seemed that if the reduction were made by heating rapidly to the boiling point, the reducing effect of the invert sugar would be so largely utilized that it could be used as an accurate measure of the invert sugar, while at the same time the objectionable reducing effect of the sucrose in other methods would be avoided. These expectations were borne out.

The curves in Figure 4 show that, after boiling commences, the copper reduced by invert sugar increases very slowly with continued boiling, while the copper reduced in the presence of sucrose increases fairly rapidly, and the data therefore confirm the general nature of Bruhns' observation.

The procedure accordingly selected for this method was to heat the solution to the boiling point in a period of 2 minutes, and then to cool by the immediate addition of cold water. Under these standard conditions points for a series of curves as shown in Figure 5 were determined, and from these Tables XI, XII, and XIII were calculated. These curves also show a linear relationship.

An inexpensive electric heater, such as the Gilmer, is convenient and can be easily adjusted for the purpose, and is a great improvement over the old gas burner because it avoids the direct application of a hot flame.

The values for zero per cent invert sugar in the presence of sucrose are extremely small—viz., 2.8 mg. for 3 grams of sucrose and 3.8 mg. for 5 grams. This indicates that the question of local overheating to which Pick (*12*) alludes cannot be serious in this method.

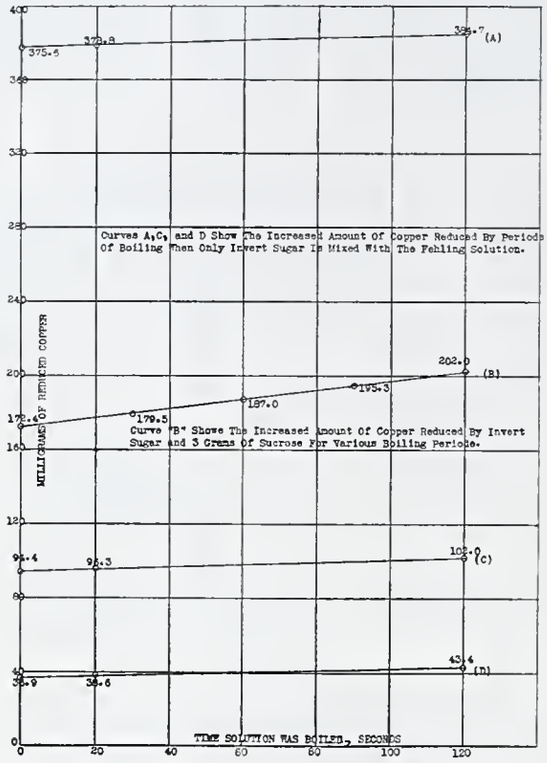

Figure 4. Effect of Boiling on Reducing Power of Invert Sugar or Mixture of Invert Sugar and Sucrose

In the description of the method below, a tolerance of 10 seconds in the heating period is given. This allows for ordinary variations in adjusting the heater and in judging the exact end point. The curves in Figure 4 show that this tolerance is without serious influence. The heating was controlled within closer limits than this in establishing the curves on Figure 5.

The basic data for this method were determined at an altitude of 3930 feet where the boiling point of water is about 96° C. It cannot be definitely stated how much variation might be found at sea level or other altitudes, although the fact that a tolerance of ±10 seconds is permitted in the method would indicate that this feature is probably of negligible importance. It would have a more decided influence in the Herzfeld method, in which the temperature of the solution is maintained at the boiling point for a protracted period of time.

The primary advantage of this method is the small correction for the reducing effect of sucrose. Other advantages are the simplicity of the procedure and the short length of time required. The solution does not boil over, as sometimes happens in the Herzfeld method.

The single disadvantage is the fact that the precipitate is finely divided and difficult to filter, in which respects it resembles but is no worse than the precipitate obtained in the Herzfeld method. More than ordinary care has to be taken in the preparation of asbestos mats which will retain all the precipitated copper.

Comparison of the Two Methods

The authors have no absolute preference between the two methods described. Both give reproducible results. Chemists who have worked with both methods generally prefer the 2-minute heating method for very small amounts of invert sugar or like its simplicity when a quick determination is required. On the other hand, they prefer the Quisumbing and Thomas method for larger amounts of invert sugar on account of the greater ease of filtering and washing the precipitate.

A detailed description of the recommended procedure follows. The Fehling solutions used in both methods are the Quisumbing and Thomas modifications.

Reagents

Neutral Lead Acetate Solution. Transfer 422.5 grams of c. p. neutral (not basic) lead acetate ($Pb(CH_3COO)_2 \cdot 3H_2O$) to a 1000-ml. flask, fill the flask about three-fourths full with water, and heat in a water bath nearly to boiling until the lead acetate is completely dissolved. Fill to the mark with water, cool to 20° C., make up to the mark again with water, and mix. The solution should have a density of approximately 55° Brix.

Oxalate–Phosphate Solution. Dissolve 5 grams of c. p. sodium oxalate and 5 grams of c. p. ammonium dihydrogen phosphate in water and make up to 100 ml.

Fehling Solution A. Dissolve 42 grams of c. p. crystallized copper sulfate in boiling water, dilute to a volume of 500 ml. at 20° C., mix, and filter. Determine the amount of copper in solution by a standard method, such as the titration of 10 ml. according to the volumetric thiosulfate method. Dilute the copper sulfate solution so that 10 ml. contain exactly 210 mg. of copper, or so that 41.2 grams of $CuSO_4 \cdot 5H_2O$ are present in 500 ml. of the solution.

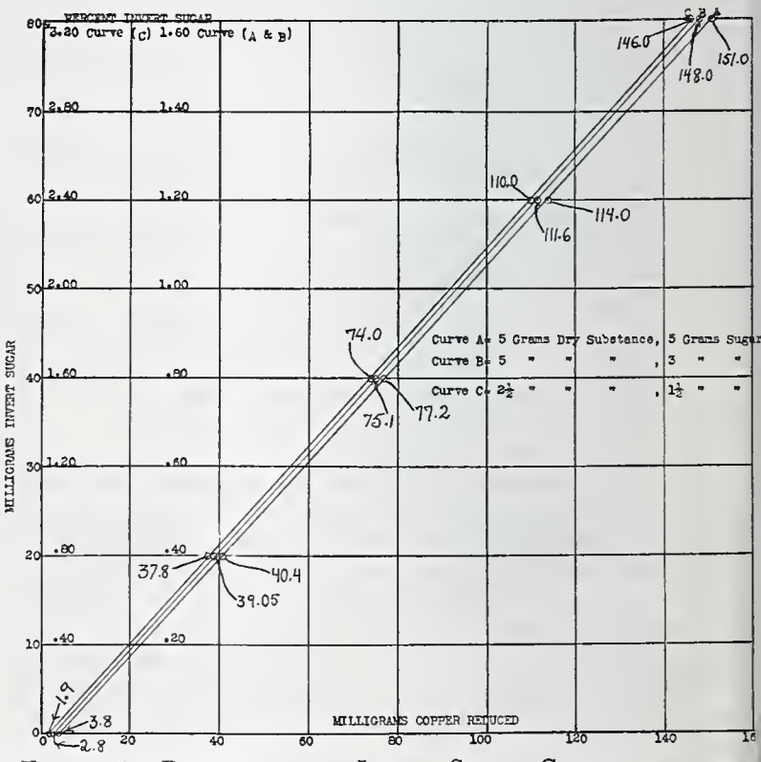

Figure 5. Percentage of Invert Sugar Calculated from Amount of Reduced Copper (Two-Minute Heating Procedure)

Fehling Solution B. Prepare a saturated solution of c. p. sodium hydroxide by dissolving 100 grams in 95 to 100 ml. of water in a Pyrex flask, and let stand for several days until the insoluble carbonates and other impurities have settled out. Then siphon off the clear solution (or filter through asbestos in a Gooch crucible if necessary), and determine its alkalinity by titrating with standard acid. Dissolve 173 grams of c. p. sodium potassium tartrate (Rochelle salt) in water in a 500-ml. flask and add the calculated amount of the sodium hydroxide solution which will contain exactly 65 grams of

Table VI. Weight of Material for Invert Sugar Determination

(To yield 5 grams of dry substance)

Brix or Dry Substance	Grams[a]	Brix or Dry Substance	Grams	Brix or Dry Substance	Grams	Brix or Dry Substance	Grams
40.0	55.0	55.0	40.0	70.0	31.4	85.0	25.9
40.5	54.3	55.5	39.6	70.5	31.2	85.5	25.7
41.0	53.7	56.0	39.3	71.0	31.0	86.0	25.6
41.5	53.0	56.5	38.9	71.5	30.8	86.5	25.4
42.0	52.4	57.0	38.6	72.0	30.6	87.0	25.3
42.5	51.8	57.5	38.3	72.5	30.3	87.5	25.1
43.0	51.2	58.0	37.9	73.0	30.1	88.0	25.0
43.5	50.6	58.5	37.6	73.5	29.9	88.5	24.9
44.0	50.0	59.0	37.3	74.0	29.7	89.0	24.7
44.5	49.4	59.5	37.0	74.5	29.5	89.5	24.6
45.0	48.9	60.0	36.7	75.0	29.3	90.0	24.4
45.5	48.4	60.5	36.4	75.5	29.1	90.5	24.3
46.0	47.8	61.0	36.1	76.0	28.9	91.0	24.2
46.5	47.3	61.5	35.8	76.5	28.8	91.5	24.0
47.0	46.8	62.0	35.5	77.0	28.6	92.0	23.9
47.5	46.3	62.5	35.2	77.5	28.4	92.5	23.8
48.0	45.8	63.0	34.9	78.0	28.2	93.0	23.7
48.5	45.4	63.5	34.6	78.5	28.0	93.5	23.5
49.0	44.9	64.0	34.4	79.0	27.8	94.0	23.4
49.5	44.4	64.5	34.1	79.5	27.7	94.5	23.3
50.0	44.0	65.0	33.8	80.0	27.5	95.0	23.2
50.5	43.6	65.5	33.6	80.5	27.3	95.5	23.0
51.0	43.1	66.0	33.3	81.0	27.2	96.0	22.9
51.5	42.7	66.5	33.1	81.5	27.0	96.5	22.8
52.0	42.3	67.0	32.8	82.0	26.8	97.0	22.7
52.5	41.9	67.5	32.6	82.5	26.7	97.5	22.6
53.0	41.5	68.0	32.4	83.0	26.5	98.0	22.4
53.5	41.1	68.5	32.1	83.5	26.3	98.5	22.3
54.0	40.7	69.0	31.9	84.0	26.2	99.0	22.2
54.5	40.4	69.5	31.7	84.5	26.0	99.5	22.1
						100.0	22.0

[a] Grams $= \frac{2200}{\text{Brix or dry substance}}$.

Table VII. Weight of Material for Invert Sugar Determination

(To yield 2.5 grams of dry substance)

Brix or Dry Substance	Grams[a]	Brix or Dry Substance	Grams	Brix or Dry Substance	Grams	Brix or Dry Substance	Grams
40.0	27.5	55.0	20.0	70.0	15.7	85.0	12.9
40.5	27.2	55.5	19.8	70.5	15.6	85.5	12.9
41.0	26.8	56.0	19.6	71.0	15.5	86.0	12.8
41.5	26.5	56.5	19.5	71.5	15.4	86.5	12.7
42.0	26.2	57.0	19.3	72.0	15.3	87.0	12.6
42.5	25.9	57.5	19.1	72.5	15.2	87.5	12.6
43.0	25.6	58.0	19.0	73.0	15.1	88.0	12.5
43.5	25.3	58.5	18.8	73.5	15.0	88.5	12.4
44.0	25.0	59.0	18.6	74.0	14.9	89.0	12.4
44.5	24.7	59.5	18.5	74.5	14.8	89.5	12.3
45.0	24.4	60.0	18.3	75.0	14.7	90.0	12.2
45.5	24.2	60.5	18.2	75.5	14.6	90.5	12.2
46.0	23.9	61.0	18.0	76.0	14.5	91.0	12.1
46.5	23.7	61.5	17.9	76.5	14.4	91.5	12.0
47.0	23.4	62.0	17.7	77.0	14.3	92.0	12.0
47.5	23.2	62.5	17.6	77.5	14.2	92.5	11.9
48.0	22.9	63.0	17.5	78.0	14.1	93.0	11.8
48.5	22.7	63.5	17.3	78.5	14.0	93.5	11.8
49.0	22.4	64.0	17.2	79.0	13.9	94.0	11.7
49.5	22.2	64.5	17.1	79.5	13.8	94.5	11.6
50.0	22.0	65.0	16.9	80.0	13.8	95.0	11.6
50.5	21.8	65.5	16.8	80.5	13.7	95.5	11.5
51.0	21.6	66.0	16.7	81.0	13.6	96.0	11.5
51.5	21.4	66.5	16.5	81.5	13.5	96.5	11.4
52.0	21.2	67.0	16.4	82.0	13.4	97.0	11.3
52.5	21.0	67.5	16.3	82.5	13.3	97.5	11.3
53.0	20.8	68.0	16.2	83.0	13.3	98.0	11.2
53.5	20.6	68.5	16.1	83.5	13.2	98.5	11.2
54.0	20.4	69.0	15.9	84.0	13.1	99.0	11.1
54.5	20.2	69.5	15.8	84.5	13.0	99.5	11.1
						100.0	11.0

[a] Grams $= \frac{1100}{\text{Brix or dry substance}}$.

NaOH, then complete the volume to 500 ml. with water. It is essential that the sodium hydroxide solution be prepared as described and that all reagents be of high purity, because the purity of the reagents and the concentration of the alkali have such a decided influence on the reaction.

de Koninck Starch Solution. Grind 2 grams of potato starch to a paste with cold water, and add to a liter of boiling water. Boil 2 or 3 minutes, and then add 8 ml. of a 10 per cent solution of potassium iodide saturated with mercuric iodide. Allow the solution to cool, pour into a tall glass cylinder, and decant the clear liquid after it has stood a day or two. Use 10 ml. as an indicator in iodometric titrations. This solution will keep almost indefinitely.

Determination

Weigh out the number of grams of material represented by the fraction 2200/per cent dry substance, which can conveniently be obtained from Table VI. This yields 5 grams of dry substance in the final determination and is the amount to be used when possible. If the amount of copper found is beyond the limit of the copper table, the determination should be repeated on 2.5 grams of dry substance, using the number of grams of material equal to 1100/per cent dry substance as given by Table VII. The determination may also be made on 2.5 grams of dry substance in the case of dilute solutions, such as thin juice, which do not fall within the range of the volumetric procedure for 5 grams of dry substance.

Dissolve in hot water, rinse into a 200-ml. flask, cool, add 10 ml. of neutral lead acetate solution, make up to the mark with water, shake well, and filter. To 100 ml. of the filtrate add 10 ml. of the oxalate–phosphate solution, shake, and filter. Measure with a pipet 25 ml. each of the Fehling solutions A and B into a 250-ml. Erlenmeyer flask, add 50 ml. of the clarified, deleaded test solution, and heat by one of the two procedures specified below.

Method I (Quisumbing and Thomas). Heat in a water bath at exactly 80° C. for exactly 30 minutes. The flask must be clamped in place so that the level of the liquid is submerged about 2 inches below the level of the water in the bath. A ring stand and clamp make a convenient arrangement for holding the flask in place during the heating period. The neck of the Erlenmeyer flask must be covered with a watch glass throughout the heating period to prevent unnecessary access of air to the solution.

Table VIII. Percentage of Invert Sugar by Quisumbing and Thomas Method

(5 grams dry substance, 5 grams sucrose—for sugar and thick juice)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%
25.0	0.00				
26.8	0.02	81.6	0.62	136.4	1.22
28.7	0.04	83.5	0.64	138.3	1.24
30.5	0.06	85.3	0.66	140.1	1.26
32.3	0.08	87.1	0.68	141.9	1.28
34.1	0.10	88.9	0.70	143.7	1.30
36.0	0.12	90.8	0.72	145.6	1.32
37.8	0.14	92.6	0.74	147.4	1.34
39.6	0.16	94.4	0.76	149.2	1.36
41.4	0.18	96.2	0.78	151.0	1.38
43.3	0.20	98.1	0.80	152.9	1.40
45.1	0.22	99.9	0.82	154.7	1.42
46.9	0.24	101.7	0.84	156.5	1.44
48.7	0.26	103.5	0.86	158.3	1.46
50.6	0.28	105.4	0.88	160.2	1.48
52.4	0.30	107.2	0.90	162.0	1.50
54.2	0.32	109.0	0.92	163.8	1.52
56.1	0.34	110.9	0.94	165.7	1.54
57.9	0.36	112.7	0.96	167.5	1.56
59.7	0.38	114.5	0.98	169.3	1.58
61.5	0.40	116.3	1.00	171.1	1.60
63.4	0.42	118.2	1.02		
65.2	0.44	120.0	1.04		
67.0	0.46	121.8	1.06		
68.8	0.48	123.6	1.08		
70.7	0.50	125.5	1.10		
72.5	0.52	127.3	1.12		
74.3	0.54	129.1	1.14		
76.1	0.56	130.9	1.16		
78.0	0.58	132.8	1.18		
79.8	0.60	134.6	1.20		

[a] % Invert sugar $= \frac{\text{Mg. Cu} - 25.0}{91.333}$.

Method II (Two-Minute Heating). Place the flask on an electric heater, adjusted with a rheostat so that the 100 ml. of solution will come to a full boil in exactly 2 minutes, within a tolerance of ±10 seconds. (Preliminary adjustment of the rheostat may be made with the use of 100 ml. of water in a

Table IX. Percentage of Invert Sugar by Quisumbing and Thomas Method

(5 grams dry substance, 3 grams sucrose—for molasses)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%
18.0	0.00				
19.9	0.02	70.4	0.56	120.9	1.10
21.7	0.04	72.2	0.58	122.7	1.12
23.6	0.06	74.1	0.60	124.6	1.14
25.5	0.08	76.0	0.62	126.5	1.16
27.4	0.10	77.8	0.64	128.3	1.18
29.2	0.12	79.7	0.66	130.2	1.20
31.1	0.14	81.6	0.68	132.1	1.22
32.9	0.16	83.5	0.70	133.9	1.24
34.8	0.18	85.3	0.72	135.8	1.26
36.7	0.20	87.2	0.74	137.7	1.28
38.6	0.22	89.1	0.76	139.6	1.30
40.4	0.24	90.9	0.78	141.4	1.32
42.3	0.26	92.8	0.80	143.3	1.34
44.2	0.28	94.7	0.82	145.2	1.36
46.1	0.30	96.5	0.84	147.0	1.38
47.9	0.32	98.4	0.86	148.9	1.40
49.8	0.34	100.3	0.88	150.8	1.42
51.6	0.36	102.2	0.90	152.6	1.44
53.5	0.38	104.0	0.92	154.5	1.46
55.4	0.40	105.9	0.94	156.4	1.48
57.3	0.42	107.8	0.96	158.3	1.50
59.1	0.44	109.6	0.98	160.1	1.52
61.0	0.46	111.5	1.00	162.0	1.54
62.9	0.48	113.4	1.02	163.9	1.56
64.8	0.50	115.2	1.04	165.7	1.58
66.6	0.52	117.1	1.06	167.6	1.60
68.5	0.54	119.0	1.08		

[a] % Invert sugar = $\frac{\text{Mg. Cu} - 18.0}{93.5}$.

Table XI. Percentage of Invert Sugar by Two-Minute Heating Method

(5 grams dry substance, 5 grams sucrose—for sugar and thick juice)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%
3.8	0.00				
5.6	0.02	60.7	0.62	115.6	1.22
7.5	0.04	62.6	0.64	117.6	1.24
9.3	0.06	64.4	0.66	119.5	1.26
11.1	0.08	66.2	0.68	121.3	1.28
13.0	0.10	68.1	0.70	123.1	1.30
14.8	0.12	69.9	0.72	125.0	1.32
16.7	0.14	71.7	0.74	126.8	1.34
18.5	0.16	73.6	0.76	128.6	1.36
20.3	0.18	75.4	0.78	130.5	1.38
22.2	0.20	77.2	0.80	132.3	1.40
24.0	0.22	79.1	0.82	134.2	1.42
25.8	0.24	80.9	0.84	136.0	1.44
27.7	0.26	82.7	0.86	137.8	1.46
29.5	0.28	84.6	0.88	139.7	1.48
31.3	0.30	86.4	0.90	141.5	1.50
33.2	0.32	88.3	0.92	143.3	1.52
35.0	0.34	90.1	0.94	145.2	1.54
36.8	0.36	91.9	0.96	147.0	1.56
38.7	0.38	93.8	0.98	148.8	1.58
40.5	0.40	95.6	1.00	150.7	1.60
42.4	0.42	97.4	1.02	152.5	1.62
44.2	0.44	99.3	1.04	154.4	1.64
46.0	0.46	101.1	1.06	156.2	1.66
47.9	0.48	102.9	1.08	158.0	1.68
49.7	0.50	104.8	1.10	159.9	1.70
51.5	0.52	106.6	1.12	161.7	1.72
53.4	0.54	108.5	1.14	163.5	1.74
55.2	0.56	110.3	1.16	165.4	1.76
57.0	0.58	112.1	1.18	167.2	1.78
58.9	0.60	114.0	1.20	169.0	1.80

[a] % Invert sugar = $\frac{\text{Mg. Cu} - 3.8}{91.80}$.

250-ml. Erlenmeyer flask.) As soon as the solution comes to a full boil, remove the flask from the heater, and cool by the immediate addition of 100 ml. of water of room temperature.

After the heating by Method I or II has been completed, filter the solution immediately or after allowing it to stand only long enough for the copper precipitate to settle, employing a Gooch crucible with an asbestos mat about 8 mm. thick. More rapid filtration and better washing can be accomplished if the liquid

Table X. Percentage of Invert Sugar by Quisumbing and Thomas Method

(2.5 grams dry substance, 1.5 grams sucrose)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%	*Mg.*	%
15.0	0.00						
15.9	0.02	52.7	0.82	89.5	1.62	126.3	2.42
16.8	0.04	53.6	0.84	90.4	1.64	127.2	2.44
17.8	0.06	54.6	0.86	91.4	1.66	128.2	2.46
18.7	0.08	55.5	0.88	92.3	1.68	129.1	2.48
19.6	0.10	56.4	0.90	93.2	1.70	130.0	2.50
20.5	0.12	57.3	0.92	94.1	1.72	130.9	2.52
21.4	0.14	58.2	0.94	95.0	1.74	131.8	2.54
22.4	0.16	59.2	0.96	96.0	1.76	132.8	2.56
23.3	0.18	60.1	0.98	96.9	1.78	133.7	2.58
24.2	0.20	61.0	1.00	97.8	1.80	134.6	2.60
25.1	0.22	61.9	1.02	98.7	1.82	135.5	2.62
26.0	0.24	62.8	1.04	99.6	1.84	136.4	2.64
27.0	0.26	63.8	1.06	100.6	1.86	137.4	2.66
27.9	0.28	64.7	1.08	101.5	1.88	138.3	2.68
28.8	0.30	65.6	1.10	102.4	1.90	139.2	2.70
29.7	0.32	66.5	1.12	103.3	1.92	140.1	2.72
30.6	0.34	67.4	1.14	104.2	1.94	141.0	2.74
31.6	0.36	68.4	1.16	105.2	1.96	142.0	2.76
32.5	0.38	69.3	1.18	106.1	1.98	142.9	2.78
33.4	0.40	70.2	1.20	107.0	2.00	143.8	2.80
34.3	0.42	71.1	1.22	107.9	2.02	144.7	2.82
35.2	0.44	72.0	1.24	108.8	2.04	145.6	2.84
36.2	0.46	73.0	1.26	109.8	2.06	146.6	2.86
37.1	0.48	73.9	1.28	110.7	2.08	147.5	2.88
38.0	0.50	74.8	1.30	111.6	2.10	148.4	2.90
38.9	0.52	75.7	1.32	112.5	2.12	149.3	2.92
39.8	0.54	76.6	1.34	113.4	2.14	150.2	2.94
40.8	0.56	77.6	1.36	114.4	2.16	151.2	2.96
41.7	0.58	78.5	1.38	115.3	2.18	152.1	2.98
42.6	0.60	79.4	1.40	116.2	2.20	153.0	3.00
43.5	0.62	80.3	1.42	117.1	2.22	153.9	3.02
44.4	0.64	81.2	1.44	118.0	2.24	154.9	3.04
45.4	0.66	82.2	1.46	119.0	2.26	155.8	3.06
46.3	0.68	83.1	1.48	119.9	2.28	156.7	3.08
47.2	0.70	84.0	1.50	120.8	2.30	157.6	3.10
48.1	0.72	84.9	1.52	121.7	2.32	158.5	3.12
49.0	0.74	85.8	1.54	122.6	2.34	159.4	3.14
50.0	0.76	86.7	1.56	123.6	2.36	160.4	3.16
50.9	0.78	87.7	1.58	124.5	2.38	161.3	3.18
51.8	0.80	88.6	1.60	125.4	2.40	162.2	3.20

[a] % Invert sugar = $\frac{\text{Mg. Cu} - 15.0}{46.0}$.

is carefully decanted from the copper precipitate, which is then washed well by decantation, and finally the contents of the flask are washed into the crucible and the washing is completed. It is unnecessary to police the flask if the same flask is used for the determination of the copper by the volumetric thiosulfate method.

Determination of Reduced Copper

Determine by a standard method, preferably the volumetric thiosulfate method.

Use of Copper Tables

Method I (Quisumbing and Thomas). If the determination is made on 5 grams of dry substance, obtain the percentage of invert sugar from Table VIII or IX. Use Table VIII for sugar or juices of high purity. Use Table IX for molasses of approximately 60 purity. Values for products of intermediate purity between sugar and molasses can be obtained most accurately by interpolation between Tables VIII and IX. If the determination is made on 2.5 grams of dry substance, use Table X, which is intended for molasses, but can be used without serious error for products of higher purity.

Method II (Two-Minute Heating). The use of Tables XI, XII, and XIII is similar to that of Tables VIII, IX, and X, respectively.

In the case of products of abnormally high invert sugar content, of which 2.5 grams of dry substance should be used,

Table XII. Percentage of Invert Sugar by Two-Minute Heating Method

(5 grams dry substance, 3 grams sucrose—for molasses)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%
2.8	0.00				
4.6	0.02	59.1	0.62	113.5	1.22
6.4	0.04	60.9	0.64	115.3	1.24
8.2	0.06	62.7	0.66	117.1	1.26
10.1	0.08	64.5	0.68	119.0	1.28
11.9	0.10	66.3	0.70	120.8	1.30
13.7	0.12	68.1	0.72	122.6	1.32
15.5	0.14	70.0	0.74	124.4	1.34
17.3	0.16	71.8	0.76	126.2	1.36
19.1	0.18	73.6	0.78	128.0	1.38
21.0	0.20	75.4	0.80	129.9	1.40
22.8	0.22	77.2	0.82	131.7	1.42
24.6	0.24	79.0	0.84	133.5	1.44
26.4	0.26	80.8	0.86	135.3	1.46
28.2	0.28	82.7	0.88	137.1	1.48
30.0	0.30	84.5	0.90	138.9	1.50
31.8	0.32	86.3	0.92	140.7	1.52
33.7	0.34	88.1	0.94	142.6	1.54
35.5	0.36	89.9	0.96	144.4	1.56
37.3	0.38	91.7	0.98	146.2	1.58
39.1	0.40	93.6	1.00	148.0	1.60
40.9	0.42	95.4	1.02	149.8	1.62
42.7	0.44	97.2	1.04	151.6	1.64
44.5	0.46	99.0	1.06	153.4	1.66
46.4	0.48	100.8	1.08	155.3	1.68
48.2	0.50	102.6	1.10	157.1	1.70
50.0	0.52	104.4	1.12	158.9	1.72
51.8	0.54	106.3	1.14	160.7	1.74
53.6	0.56	108.1	1.16	162.5	1.76
55.4	0.58	109.9	1.18	164.3	1.78
57.3	0.60	111.7	1.20	166.2	1.80

[a] % Invert sugar = $\frac{\text{Mg. Cu} - 2.8}{90.75}$.

Table XIII. Percentage of Invert Sugar by Two-Minute Heating Method

(2.5 grams dry substance, 1.5 grams sucrose)

Copper	Invert[a] Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance	Copper	Invert Sugar on Dry Substance
Mg.	%	*Mg.*	%	*Mg.*	%
1.9	0.00				
3.7	0.04	57.7	1.24	111.8	2.44
5.5	0.08	59.5	1.28	113.6	2.48
7.3	0.12	61.3	1.32	115.4	2.52
9.1	0.16	63.1	1.36	117.2	2.56
10.9	0.20	64.9	1.40	119.0	2.60
12.7	0.24	66.7	1.44	120.8	2.64
14.5	0.28	68.5	1.48	122.6	2.68
16.3	0.32	70.3	1.52	124.4	2.72
18.1	0.36	72.1	1.56	126.2	2.76
19.9	0.40	73.9	1.60	128.0	2.80
21.7	0.44	75.7	1.64	129.8	2.84
23.5	0.48	77.6	1.68	131.6	2.88
25.3	0.52	79.4	1.72	133.4	2.92
27.1	0.56	81.2	1.76	135.2	2.96
28.9	0.60	83.0	1.80	137.0	3.00
30.7	0.64	84.8	1.84	138.8	3.04
32.5	0.68	86.6	1.88	140.6	3.08
34.3	0.72	88.4	1.92	142.4	3.12
36.1	0.76	90.2	1.96	144.2	3.16
37.9	0.80	92.0	2.00	146.0	3.20
39.7	0.84	93.8	2.04	147.8	3.24
41.5	0.88	95.6	2.08	149.6	3.28
43.3	0.92	97.4	2.12	151.4	3.32
45.1	0.96	99.2	2.16	153.2	3.36
46.9	1.00	101.0	2.20	155.0	3.40
48.7	1.04	102.8	2.24	156.8	3.44
50.5	1.08	104.6	2.28	158.6	3.48
52.3	1.12	106.4	2.32	160.4	3.52
54.1	1.16	108.2	2.36	162.2	3.56
55.9	1.20	110.0	2.40	164.0	3.60

[a] % Invert sugar = $\frac{\text{Mg. Cu} - 1.9}{45.03}$.

Tables X and XIII can be considerably extrapolated with reasonable accuracy by means of the formulas at the bottom of the tables. This must not be carried to too great an extreme—i. e., to the region where the amount of invert sugar present is sufficient to reduce the Fehling solution completely.

Care must be taken not to confuse the use of the various tables.

Blank Determinations

Before making any invert sugar determinations with new solutions, or with old solutions that have stood for any length of time, conduct one or more blank determinations as follows: Weigh out 12 grams of sugar of high purity, free from reducing sugars, dissolve in water, and make up to a volume of 200 ml. Make an invert sugar determination with 50 ml. of this solution (3 grams of sucrose) according to the standard procedure. The amount of copper obtained should, according to the tables, be 18.0 mg. for the Quisumbing and Thomas heating method, or 2.8 mg. for the 2-minute heating method. If the amount obtained differs from the theoretical value by more than 3 or 4 mg., there has been some fault in the technic or in the preparation or condition of the reagents, which it should be possible to correct.

Conclusions

Present methods for the determination of small amounts of invert sugar in the presence of sucrose are not readily adaptable to products of varying concentration and purity and are open to various objections. As a result of investigations, a procedure applicable to all beet sugar factory products is described and two methods of carrying out the copper reduction are recommended.

The following conclusions are drawn: The amount of the test solution used for the reduction of 50 ml. of Fehling solution should contain 5 grams of dry substance; it is not practical to reduce the strength of the Fehling solution; the solution should be clarified with neutral lead acetate and is best deleaded by a solution of sodium oxalate and ammonium dihydrogen phosphate; and the Fehling solutions must be prepared from reagents of high purity and the concentrations must be carefully controlled.

Acknowledgment

The authors' thanks are due to R. J. Brown for helpful suggestions advanced during the development of the methods.

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Japanese Import and Export License System for Sulfate of Ammonia Abolished. The licensing regulations, promulgated in Japan on December 8, 1931, to govern the importation and exportation of sulfate of ammonia, and enforced on imports with effect from January 15, 1932, were canceled on December 6, according to a cablegram received in the Department of Commerce.

Determination of Hydrocyanic Acid in Air and in Air–Carbon Dioxide Mixtures

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In fumigating a tree with hydrocyanic acid, it is covered with a canvas tent, and the desired amount of liquid acid introduced beneath the tent. The canvas tents are by no means gas-tight, and consequently there is a rapid decrease in the concentration of hydrocyanic acid. The rapidity of decrease depends upon numerous factors, including the ratio of tent surface to tent volume, the "tightness" of the canvas under the prevailing conditions of humidity, the density of the foliage, and the velocity of the air currents. In a typical fumigation, an initial concentration of about 15 mg. per liter was reduced to 1 mg. per liter in about 17 minutes (see Figure 1).

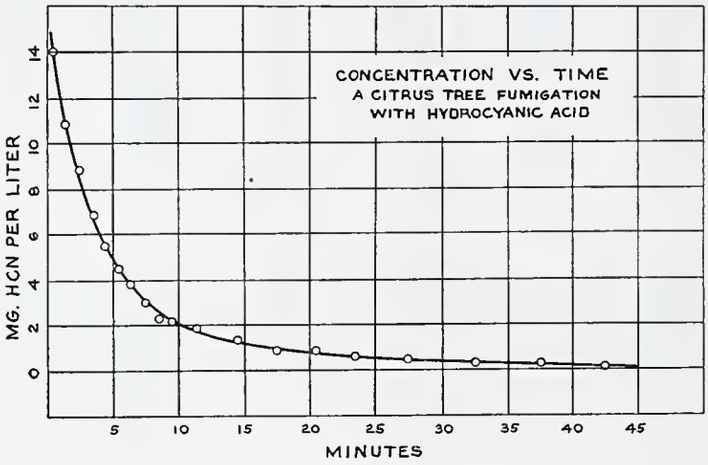

Figure 1

In order to determine satisfactorily the time-concentration relationship during such a field fumigation, it is necessary to obtain gas samples in rapid succession, and each sample must be of sufficient volume to make possible a reasonably accurate analysis. The apparatus here described has proved admirably adapted for this work, and the author believes that it may be used to advantage in other cases where the requirements are similar.

Description of Apparatus

A simple type of apparatus has been developed for making analyses during field fumigations with hydrocyanic acid. The principle of operation is to absorb the hydrocyanic acid from a continuous current of the gas mixture, the volume of which is proportional to the duration of the sampling period and to the rate of flow, as measured by a capillary-tube flowmeter (*1*). The chief point of interest in the present apparatus lies in the facility with which samples may be taken in rapid succession without interrupting the flow of the mixed gases through the sampling tube, together with the relative simplicity of construction and manipulation. A simple flow diagram of this apparatus is shown in Figure 2.

For field work the air exhaust is obtained by connection to the intake manifold of a motor car engine, which is kept in operation during a series of analyses. In the laboratory, a water exhaust pump or a laboratory "oil" pump may be used. The surge tank eliminates sudden fluctuations which might be caused by irregular operation of the exhaust pump. The needle valve serves to adjust the rate of flow accurately to a definite value, as measured by the calibrated flowmeter. By properly manipulating the four glass stopcocks, the gas stream may be quickly diverted to either of the two absorbers, and by following a definite time schedule, the stream may thus be divided into separate portions of known volume.

The apparatus is illustrated in Figure 3. The wooden stand, *A*, supports and protects the capillary-tube flowmeter. The absorbing bottles, *C* and *D*, are supported by separate, removable wooden stands, *E*, and are selected to fit easily the two rubber stoppers which carry the gas delivery and exit tubes, together with the glass stopcocks, *B*, which direct the flow of gas to either of the absorbing bottles. While the gas stream is passing through one absorbing bottle, the other one may be replaced by a bottle containing a fresh portion of absorbing solution. In this manner a continuous series of samples may be taken without interrupting the flow of gas through the sampling tube. It is quite easy for one operator to take samples at the rate of one per minute, and greater speed may be attained if desired.

The flowmeter is of the capillary-tube type, and as the hydrocyanic acid–air mixture passes through the flowmeter before entering the absorbers it is necessary to guard against possible loss of hydrocyanic acid by absorption in the manometer liquid or in rubber connectors. The capillary tube is held in place by rubber connectors, but the glass parts are kept close together in order to minimize contact between the gas and the rubber. A light petroleum oil is used in the manometer, as hydrocyanic acid is said to be practically insoluble in such an oil. One leg of the manometer is connected through a glass stopcock to a wider side tube which is open to the atmosphere. With the use of this side tube, the level of oil in the manometer tubes may quickly and easily be adjusted to a fixed zero mark. For ordinary use it is necessary only to calibrate the flowmeter at one fixed mark, and then adjust the rate of flow during each experiment to give this

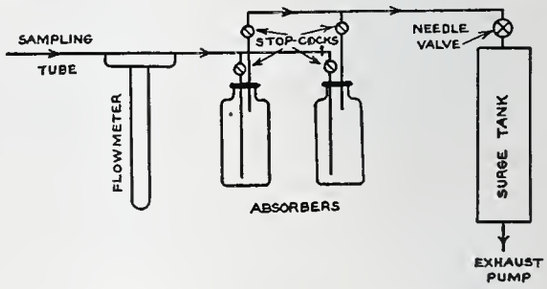

Figure 2. Flow Diagram of Analysis Apparatus

same manometer reading. The temperature of the oil in the manometer may be determined and the appropriate temperature correction applied. A small correction may also be applied for the temporary decrease in the rate of gas flow which occurs when the gas space above the absorbing liquid, in a fresh bottle of absorbent, is first opened to the exhaust line. In order to allow for the rather slow drainage of oil from the walls of the manometer tubes, the flow of gas should be started about 10 minutes before beginning a series of analyses.

In addition to its usefulness in making analyses during field

fumigations, this apparatus has proved to be very convenient for laboratory work. It has been used in the determination of hydrocyanic acid in admixture with carbon dioxide and air.

Analytical Methods

A well-known method for determining hydrocyanic acid in air consists in absorbing it in dilute sodium hydroxide solution and titrating with standard silver nitrate solution. This method seems to be convenient and reliable, and the end point is sharp if the titration is made with favorable conditions of illumination, such as are described below. For such an analysis the hydrocyanic acid is absorbed in 100 cc. of 2 per cent sodium hydroxide solution, 5 cc. of 2 per cent potassium iodide solution are added, and the titration is made with standard silver nitrate solution containing approximately 3 grams of silver nitrate per liter. The volume of the gas sample is adjusted to provide enough hydrocyanic acid for a satisfactory titration, and it is bubbled through the absorbing solution at the rate of about one liter per minute.

In this method of analysis the addition of potassium iodide increases the sharpness and reliability of the end point, which is indicated by the first permanent turbidity of the solution. However, the end point is somewhat difficult to see unless the illumination is favorable. Daylight is much more satisfactory than ordinary artificial illumination. The author has found that the end point is quite sharp when the titration is performed in semi-darkness, with a condensed beam of light passing through the solution in a generally horizontal direction. Satisfactory results may be obtained by the use of a

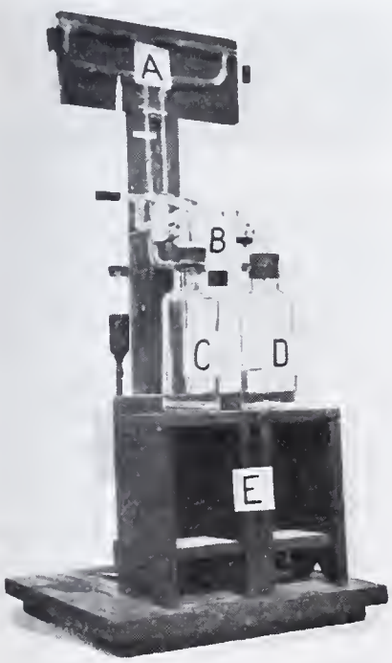

Figure 3. Analysis Apparatus

focusing flashlight, or the more powerful beam from a microscope illuminator. With such illumination a slight excess of silver nitrate produces a distinct Tyndall effect. The reaction may be expressed by the equation:

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3$$

A second method of analysis, which has been used extensively, involves the absorption of the hydrocyanic acid in a 2 per cent sodium carbonate solution, with subsequent titration with standard iodine solution (*2*). The author's results were somewhat irregular when this method of analysis was used, and it was concluded that this might be due to a variable amount of reaction between the iodine and the sodium carbonate solution itself. Subsequent experiments confirmed this expectation. If the iodine solution is added without stirring, and considerable opportunity is allowed for it to react with the sodium carbonate solution, the titration may consume a 30 per cent excess of iodine. If the iodine solution is added slowly, with very efficient stirring, the results seem to be consistent and in agreement with those of silver nitrate titrations. However, any intermediate result can be obtained, and unless precautions are taken it is comparatively easy to incur errors of 5 or 10 per cent. Satisfactory analyses may be made by absorbing the hydrocyanic acid in about 100 cc. of 2 per cent sodium carbonate solution, adding 10 cc. of

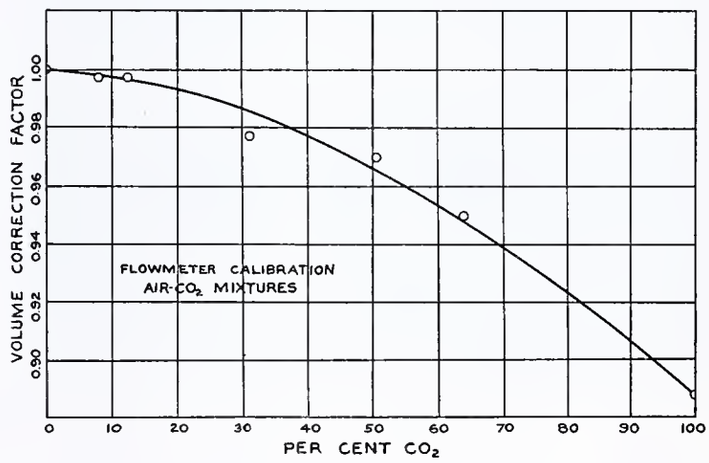

Figure 4

10 per cent potassium iodide solution and 5 cc. of 2 per cent starch solution, then titrating with standard iodine solution, with efficient stirring. The reaction may be expressed by the equation:

$$NaCN + I_2 = NaI + CNI$$

According to another well-known method of analysis, the hydrocyanic acid–air mixture is bubbled through sodium bicarbonate solution which contains a measured amount of standard iodine solution, together with potassium iodide and starch. The analysis is made by determining the volume of the gas mixture which is required just to decolorize the absorbing solution. A few comparative tests show that this method yields results which are in agreement with those of analyses by the two methods described above. Although a sodium bicarbonate solution is not, of itself, a satisfactory absorbent for hydrocyanic acid, the hydrocyanic acid will be removed from air in an efficient manner so long as free iodine is present in the solution.

Determination of Hydrocyanic Acid in Carbon Dioxide–Air Mixtures

In performing a series of experiments to determine the toxicity to red scale of hydrocyanic acid–carbon dioxide–air mixtures, the problem arose of determining hydrocyanic acid in such mixtures. The presence of carbon dioxide makes necessary certain precautions in the measurement of the gas volume. If the gas is measured over water in an aspirator bottle, it must be kept in mind that carbon dioxide is moderately soluble in water. If the gas volume is determined by its rate of flow through a capillary-tube flowmeter, it is necessary to take into account the effect of the carbon dioxide on the calibration of the flowmeter. Moreover, carbon dioxide may be too readily absorbed by the solution which is used to absorb hydrocyanic acid, or it may interfere with the subsequent titration of cyanide.

Table I. Determination of Hydrocyanic Acid in Carbon Dioxide–Air Mixtures

Carbon Dioxide	Sample Volume	Hydrocyanic Acid Total	Hydrocyanic Acid Per liter
%	*Liters*	*Mg.*	*Mg.*
0.0	4.43	6.73	1.52
100.0	3.93	5.90	1.50
47.0	4.29	5.46	1.27
27.0	4.37	5.54	1.27
12.4	4.40	5.75	1.31
7.0	4.41	5.85	1.33
0.0	4.42	5.70	1.29
7.0	4.41	5.76	1.31
12.4	4.40	5.63	1.28
8.0	4.41	4.23	0.96
0.0	4.42	4.20	0.95
8.0	4.41	3.64	0.83
0.0	4.42	3.63	0.82
0.0	4.42	2.92	0.66
8.0	4.41	2.92	0.66

It appeared that under these circumstances hydrocyanic acid might be determined satisfactorily by absorption in 2 per cent sodium carbonate solution, with subsequent titration with standard iodine. This plan contemplated that the volume of gas mixture would be determined by measuring its rate of flow through a flowmeter which had been calibrated previously for carbon dioxide–air mixtures. The calibration curve for this purpose is shown in Figure 4. This curve is strictly applicable only to the flowmeter for which it was determined, and each flowmeter which is to be used for this purpose should be individually calibrated.

A solution of hydrocyanic acid in water, of a definite concentration and at a definite temperature, has a definite hydrocyanic acid vapor pressure. This means that it will produce the same volume concentration of hydrocyanic acid in any indifferent gas which is brought into intimate contact with the solution. Therefore, if pure carbon dioxide is slowly bubbled through such a solution, it will acquire the same volume concentration of hydrocyanic acid as will a current of air which is passed through the same solution. By the use of this device the same concentrations of hydrocyanic acid in air and in various carbon dioxide–air mixtures have been produced, and the method of analysis has been checked by analyzing the mixtures. Results obtained in this manner are given in Table I, grouped in such manner that the results in column 4 would be identical within each group if there were no errors of any kind during the experiments. Considering the fact that there are probably other inaccuracies in addition to those of analysis, the results indicate that this method is suitable for the determination of hydrocyanic acid in carbon dioxide–air mixtures.

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Received July 28, 1932.

Determination of Small Quantities of Antimony in Solder in Presence of Iron

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This laboratory is called upon to analyze numerous samples of scrap solder which consist chiefly of tin and lead, but which are contaminated with as much as 5 per cent of iron. The presence of iron interferes with the titration of antimony by the usual bromate method, particularly if the amount of iron in the sample is more than 0.1 per cent. A method has therefore been worked out which eliminates this difficulty.

In reviewing the literature it was found that very little information had been recorded on the titration of antimony in the presence of iron. However, Rowell (*1*) in his method of direct estimation of antimony by the bromate method notes that the presence of 1 per cent iron increases the results by about 0.02 per cent. He gives no definite figures with larger quantities of iron.

The following procedure has given satisfactory results when as much as 15 per cent of iron is present in the sample:

Dissolve a 3-gram sample in 15 to 20 cc. of hot concentrated sulfuric acid in a 250-cc. Erlenmeyer flask. Cool the solution and add carefully 50 cc. of concentrated hydrochloric acid. Add about 0.5 gram of potassium chlorate to oxidize the iron and expel the chlorine by boiling. Cool the solution and add 20 to 25 cc. of phosphoric acid, sp. gr. 1.37, and then 3 to 4 grams of sodium sulfite. Allow the solution to stand at a temperature of about 60° C. for 15 minutes and expel the excess sulfur dioxide by boiling in a current of carbon dioxide or air for 5 to 10 minutes. Add about 50 cc. of water, and titrate at about 60° C. with 0.033 *N* potassium bromate solution which has been standardized against metallic antimony using methyl orange as indicator.

About the same quantity of iron should be present in the antimony solution used for standardizing the bromate as is present in the sample for analysis. The iron may be added as ferrous or ferric sulfate and the process of solution, reduction, and titration conducted in the same manner as in a regular determination. The methyl orange indicator should be added toward the end of the titration, having ascertained the approximate amount of bromate required by a preliminary test. The color change at the end point is readily detected, since a dilute phosphoric acid solution is only faintly colored by the usual quantities of iron occurring in scrap solder. The amount of bromate required to destroy the methyl orange color is very slight, the correction usually being approximately 0.1 cc. which is deducted from the number of cubic centimeters used in titrating.

Table I. Results of Experimental Analyses

Iron Taken as $FeSO_4.7H_2O$	Solder Taken	Antimony Taken	Total Antimony Present	Antimony Found
Gram	*Grams*	*Gram*	*Gram*	*Gram*
0.1	3.0[a]	0.0300	0.0309	0.0310
0.16	3.0[a]	0.0198	0.0207	0.0206
0.20	3.0[a]	0.0498	0.0507	0.0500
0.30	3.0[a]	0.0104	0.0113	0.0106
0.14	3.0[a]	0.0400	0.0405	0.0394
0.10	3.0[a]	0.0250	0.0259	0.0254
0.16	2.2[b]	0.0050	0.0053	0.0058
0.4	3.0[c]	0.0251	0.0269	0.0268
0.6	3.0[c]	0.0321	0.0339	0.0344
0.4	3.0[d]	0.0141	0.0153	0.0148
0.5	3.0[d]	0.0300	0.0312	0.0302

[a] Antimony content 0.03%.
[b] Antimony content 0.015%.
[c] Antimony content 0.06%.
[d] Antimony content 0.04%.

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Determination of the Diastatic Activity of Honey

H. A. Schuette and R. J. Pauly,[1] University of Wisconsin, Madison, Wis.

It has been pointed out by others (*4*) that a high degree of accuracy can be obtained in the determination of the diastatic activity of honey by the current German procedure (*1*, *2*) only if attention be given to the pH of the reaction mixtures. Attempts to apply this newer technic unexpectedly brought forth the observation that still other factors enter the picture—the quality or age of the soluble starch which is employed as substrate and the interpretation of the starch-iodine end point.

In this study five comb honeys were used, from which the honey itself was strained in the laboratory without the use of any external heat. Six soluble starch solutions, either personally prepared from crude starch or from commercial products, served as substrates.

Table I. Record of Experimental Soluble Starch Solutions

	Starch	pH of 1% Solution	Description
1.	Mallinckrodt	6.18	Of recent purchase. Boiled 3 min.
2.	Mallinckrodt	5.76	Kept at boiling point of water for 0.5 hr.
3.	Merck	5.93	"According to Lintner." About 10 years old
4.	Kahlbaum	5.17[a]	At least 15 years old
5.	Kahlbaum	6.18	Preceding starch washed with 2% NH_4OH soln. and then water, after which it was dried
6.	Lintner (*3*)	5.67	Potato starch digested 7 days at room temperature with 7.5% HCl soln.
7.	Small (*5*)	6.18	20 grams potato starch boiled 10 min. with ethyl alcohol containing 0.75% HCl
8.	Small (*5*)	6.27	Same treatment as preceding starch except 1% HCl concentration

[a] A solution made from starch taken from the upper layers in the bottle showed a pH of 4.22.

Phosphate buffer solutions were made by mixing 0.067 *M* solutions of orthophosphoric acid and its salts in the proportions given in Table II. The selection of that buffer mixture which is necessary to hold the pH of the various tubes near the optimum—5.26 to 5.30 as recommended by Lothrop and Paine (*4*)—will, of course, depend upon the pH of the honey solution already prepared as well as that of the substrate solution. If a careful selection of solutions is made, the 2 cc. of buffer solution which are added to each tube are sufficient to hold the pH of the series within a ±0.03 variation. Should more exact control be desired, it will be necessary to vary the amount of buffer solution added to each tube in proportion to the amount of honey in each, but because of the time involved this is not recommended in routine control work.

Table II. Volume Composition of Phosphate Buffer Solutions

pH	H_3PO_4	KH_2PO_4	$Na_2HPO_4 \cdot 12H_2O$
5.14	1	10.0	1
5.17	1	7.5	1
5.33	1	5.0	1
5.50	1	2.0	1
5.63	1	1.0	1

After several variations of procedure were experimented with throughout this investigation, the method given below was adopted as leading to the best reproducible results with a minimum of exacting technic. It embodies several departures from the original Gothe method (*2*).

Dissolve a 10-gram sample of honey in approximately 70 cc. of freshly boiled, and then cooled, distilled water. Neutralize the resulting solution with 0.05 *N* sodium hydroxide, using 2 drops of 1 per cent phenolphthalein indicator solution and taking as end point that at which the pink coloration persists for at least one minute, and then treat with 6 cc. of 0.02 *N* hydrochloric acid to bring the honey solution back to approximately optimum conditions at this point. (This volume of dilute hydrochloric acid will usually bring the pH of the solution within the limits 4.8 to 5.5, depending upon how accurately the end point of the titration has been determined in the presence of the phenolphthalein, and also, possibly, upon the nature of the honey itself.) Complete the volume of the whole to 100 cc., determine its pH with the aid of a quinhydrone electrode, and select the appropriate buffer solution for the reaction tubes on the basis of these measurements.

Table III. Preparation of Tubes for Determination of Diastase Value

Tube	Honey Solution (10 per cent)	Substrate[a] Mixture	Sterile Water (q. s. ad 16 cc.)	Diastase Value
	Cc.	*Cc.*	*Cc.*	
1	8.0	7.5[b]	0.5	6
2	7.0	7.5	1.5	7
3	5.5	7.5	3.0	9
4	4.5	7.5	4.0	11
5	3.6	7.5	4.9	14
6	2.8	7.5	5.7	18
7	2.2	7.5	6.3	23
8	1.7	7.5	6.8	29
9	1.3	7.5	7.2	39
10	1.0	7.5	7.5	50

[a] This mixture consists of 5 cc. soluble starch solution, 0.5 cc. 0.1 *N* NaCl solution, and 2 cc. of the 0.067 *M* phosphate buffer solution of appropriate pH.

[b] This tube may be omitted from the series if the honey under examination is an authentic one. If a lower limit must be set up because of a sample naturally poor in diastatic activity, the volume of substrate may be reduced.

Fill ten test tubes, rather than twelve as recommended by Gothe (*2*), with the mixture as shown in Table III. Thoroughly mix the contents of each tube, place the entire group in a water bath maintained at a temperature of 45° to 47° C. for one hour, gently agitating the tubes every 10 minutes, after which cool them rapidly by immersing in a bath of cold water. Immediately add 1 drop of 0.1 *N* iodine test solution, mix thoroughly, and note the colors obtained. Finally, because it is sometimes difficult to reach a decision as to the end point, add a second drop of the iodine solution, shake, and again note the colors. Select the last tube which shows a true purple color changing to a red upon the addition of the second drop of iodine solution as the basis for calculating the diastase value, or select that tube having a true purple color immediately preceding the first one in the series in which a true blue color was developed with 1 drop of the iodine solution, as lilac and violet colors often appear before purple. These can be eliminated only by the addition of a second drop of iodine, whereas the true blue color of iodo-starch is easily discernible from wines, lilacs, and purples.

Table IV. Selection of Starch-Iodide End Point

Tube	Colorations Observed: Experiment 4 Drops Iodine 1	Experiment 4 Drops Iodine 2	Experiment 17 Drops Iodine 1	Experiment 17 Drops Iodine 2	Experiment 26 Drops Iodine 1	Experiment 26 Drops Iodine 2
4	...	...	...	...	Brown	Red
5	Brown	Brown	Yellow	Brown	Light wine	Red
6	Wine	Red	Light brown	Brown	Wine	Red
7	Purple	Dark wine	Light wine	Brown	Purple	Red
8	Blue	Dark purple	Wine	Red	Blue	Purple
9	Blue	Blue	Purple	Violet	Blue	Blue
10	Blue	Blue	Blue	Purple	Blue	Blue

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Table V. Diastase Value of Honey as Affected by Kind of Soluble Starch Used

Floral source	Honey acidity (Calcd. as formic)	Method	Starch[a]	Diastase Value as Shown by Iodine Test Solution Added 1 drop	2 drops	Reaction Tubes pH range
	%					
Clover	0.185	Lothrop-Paine	4	39	..	5.32–5.31
		Pauly	2	29	39	5.28–5.29
		Gothe	1	23.8	..	5.89–4.71
			Range	23–39		
Buckwheat	0.212	Lothrop-Paine	1	23	23	5.29–5.31
		Pauly	1	23	29	5.25–5.27
		Gothe	1	14	..	5.38–4.76
			Range	14–23	23–29	
Tulip-poplar	0.183	Pauly	2	29	29	5.32–5.32
			8	14	18	5.26–5.25
		Gothe	1	18	..	6.61–4.75
			Range	14–29	18–29	
Alfalfa	0.122	Pauly	2	39	50	5.31–5.33
			8	23	23	5.26–5.29
			4	29	39	5.24–5.26
			5	29	39	5.24–5.26
		Gothe	1	23	..	5.42–4.58
			Range	23–39	23–50	
Clover	0.188	Pauly	2	50	50+	5.28–5.30
			8	29	29	5.33–5.25
		Gothe	1	39	..	5.76–4.49
			Range	29–50	29–50+	

[a] Numbers in this column refer to starch solutions recorded in Table I.

The data obtained in the application of the above-described mode of procedure for the determination of the diastase values of honey are shown in Table V. The influence exerted by the quality of the soluble starch, upon the observed diastase values, as well as the interpretation of the end point of the reaction when expressed in terms of quantity of iodine test solution used, are so obvious as hardly to require comment. However, in analyzing the data statistically, it appears that a minimum variation of 64 per cent and a maximum of 100 were found in the diastase value of the honeys under examination. Quantitatively these figures have little significance because the survey is probably insufficient with respect to number of honeys to which the modified technic has been applied. Qualitatively, however, they show that the character of the soluble starch which serves as substrate is a factor which may easily nullify the results of a determination of the diastatic activity of a honey which has otherwise been carried out with meticulous attention to detail. A standard starch is obviously necessary for this work.

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A Device for the Calibration of the Variable-Deviation Spectroscope

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The calibration of the variable-deviation spectroscope can be simplified by the device shown in the accompanying illustrations, which applies to the spectroscope the registration system of the mirror galvanometer and allows the telescope deviations to be read off on a long illuminated scale in place of the arc of a graduated circle.

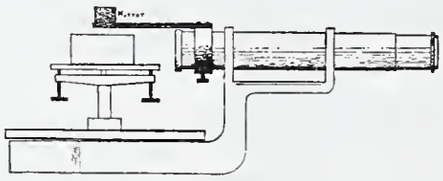

Figure 1

Figure 1 shows a bar clamped to the telescope of a spectroscope, with its end brought forward over the prism. A mirror about 2 cm. square is mounted perpendicular to the bar in such a position that the axis of rotation of the telescope lies in the plane of the mirror. A projector casts upon the mirror the vertical image of a hair, which is reflected to a scale at a convenient distance from the spectroscope. The projector, spectroscope, and scale are fastened rigidly in relation to one another, as shown in Figure 2, and calibration is carried out on the scale in the usual way.

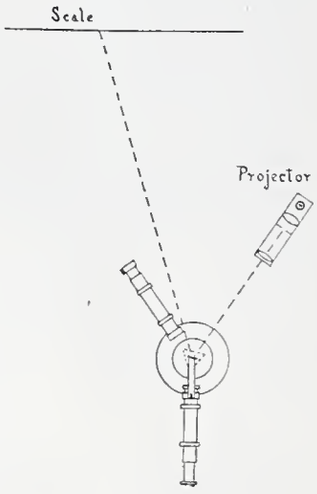

Figure 2

The deviation readings of the telescope can be spread out on the scale to any desired extent by increasing the distance between mirror and scale, and at the same time the compression of the red end of the spectrum can be counteracted by arranging the parts of the system so that the beam from the mirror strikes the scale at right angles when the telescope is at the extreme violet end of the spectrum. With a flat scale, the readings will vary as the tangent of twice the angle of telescope deviation, and will widen out rapidly as the beam strikes the scale more obliquely.

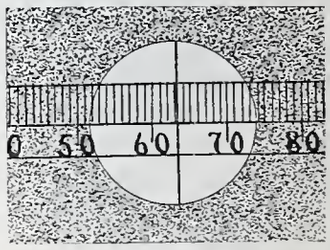

Figure 3

The projector can easily be made from a 6-volt tail-light bulb, the condensing lens of a flashlight, and a small reading lens. A 6- to 8-volt bell-ringing transformer will supply sufficient current to operate the bulb at full capacity. The image of the hair on a bright circle of light is produced by a hair stretched across an 8-mm. round hole in a small piece of sheet brass, and cemented at its ends to the brass. The lighted circle surrounding the image of the hair allows the adjacent numbers on the scale to be read, as shown in Figure 3. The expense of the whole device is nominal, and it has proved a great convenience in quickly picking up desired lines in the spectroscope.

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Determination of Furfural Produced from Hardwoods

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THE standard method for the determination of pentoses and pentosans in plant materials (*1*, *5*, *6*) involves the distillation of the sample with 12 per cent hydrochloric acid until no more furfural is produced, as indicated by the absence of a pink coloration with aniline acetate. The distillate is treated with phloroglucinol to produce a precipitate of indefinite composition which may be determined gravimetrically. Because of the empirical nature of this method and the length of time consumed in its operation, several alternative methods have been suggested. The use of thiobarbituric acid as a precipitant has been studied by Dox and Plaisance (*2*); the potentiometric titration of the furfural in acidified potassium bromide solution with potassium bromate has been proposed by Pervier and Gortner (*7*); and the use of excess bromine to react with the furfural and subsequent estimation of the unused bromine was studied by Powell and Whittaker (*8*) and recently used by Kline and Acree (*4*).

The primary object of the work recorded in this paper was the determination of the quantity of furfural produced from six species of American hardwoods. Preliminary to these determinations, a comparison of the four above-mentioned methods for the estimation of furfural was made on pure furfural samples. And further, distillations of pure furfural by means of the standard method with 12 per cent hydrochloric acid and also with 12 per cent hydrochloric acid and steam were made to contrast the relative amount of destruction in these procedures. On the basis of these comparisons the furfural produced by acid-steam distillation of the hardwood samples has been determined by the volumetric potassium bromate–bromide method of Powell and Whittaker (*8*).

Determination of Furfural

In comparing the quantitative methods of estimation, the furfural was purified by distilling technical furfural at a pressure of 16 to 20 mm. four or five times until an almost colorless distillate was obtained. Five-gram samples were immediately dissolved in water and made up to 500 cc. from which 5-cc. aliquot portions were used in the following determinations:

Phloroglucinol or A. O. A. C. Method. A quantity of phloroglucinol about double the amount necessary for the furfural present was dissolved in 12 per cent hydrochloric acid and added to the sample with stirring. The solution turned yellow and then a green precipitate appeared which grew darker until it became nearly black. After making the solution up to 400 cc. with 12 per cent hydrochloric acid and allowing it to stand overnight, the precipitate was collected on a tared Gooch, washed with 150 cc. of water, and dried at 100° C. for 4 hours. After weighing the precipitate, the amount of furfural recovered was calculated by means of Kröber's (*5*, *6*) formulas.

Thiobarbituric Acid Method. To the sample of pure furfural, made up to 200 cc. with 12 per cent hydrochloric acid, was added the precipitant consisting of thiobarbituric acid, slightly in excess of the equivalent amount, also dissolved in 12 per cent hydrochloric acid. The final volume was made up to 400 cc. with 12 per cent hydrochloric acid and allowed to stand overnight to insure complete precipitation. The precipitate, which filtered slowly, was collected on a tared Gooch and dried at 100° C. The weight of furfural was calculated on the basis of a reaction ratio of one molecule of furfural to one of thiobarbituric acid.

Volumetric Potassium Bromate–Bromide Method. Following the method suggested by Powell and Whittaker and since used by others, 25-cc. portions of approximately 0.1 *N* potassium bromate–bromide were pipetted into four glass-stoppered bottles. Into two of these the samples made up to 200 cc. with 12 per cent hydrochloric acid were added and into the other two, 200 cc. of 12 per cent hydrochloric acid were added for blank runs. After standing for one hour in the dark, 10 cc. of 10 per cent potassium iodide were added and the liberated iodine was titrated with 0.1 *N* sodium thiosulfate. The number of cubic centimeters required by the sample subtracted from the number required for the blank was a measure of the furfural present.

In an attempt to employ the potentiometric method proposed by Pervier and Gortner great difficulty was found in determining the end point, and erratic and often high results were obtained. This observation has been made also by Youngburg and Pucher (*12*). Consequently it was not used in further work.

A comparison of the averages of results for the three methods given in Table I (100.17, 102.0 and 102.88 per cent) shows that the standard phloroglucinol method gave practically theoretical results, while the latter two were slightly above the theoretical which is in close agreement with the results for these methods recorded by the original authors (*2*, *8*). The widest variations in the errors observed in the different methods of analyzing weighed portions of furfural were about 2 per cent with phloroglucinol, 1 per cent with thiobarbituric acid, and 1.2 per cent with potassium bromate–bromide. If in contrasting these three methods the advantages of greater simplicity, economy of time, and equal constancy of results are considered, then the volumetric method seems to be superior to either of the gravimetric methods.

Table I

Sample	Furfural Used	Precipitant Used	Precipitate	Furfural Found	Furfural Recovered
	Gram	*Gram*	*Gram*	*Gram*	%
			Phloroglucinol method		
1	0.0574	0.390	0.1054	0.0573	99.82
2	0.0574	0.389	0.1050	0.0571	99.48
3	0.0574	0.390	0.1074	0.0584	101.74
4	0.0574	0.390	0.1051	0.0572	99.65
					Av. 100.17
			Thiobarbituric acid method		
1	0.0575	0.132	0.1367	0.0591	102.78
2	0.0575	0.132	0.1352	0.0585	101.73
3	0.0575	0.132	0.1353	0.0585	101.73
4	0.0575	0.132	0.1356	0.0586	101.91
					Av. 102.04

Volumetric potassium bromate–bromide method

Sample	Furfural Used	0.1 *N* $Na_2S_2O_3$	Furfural Found	Furfural Recovered
	Gram	*Cc.*	*Gram*	%
1	0.0508	21.69	0.0521	102.55
2	0.0508	21.67	0.0520	102.36
3	0.0508	21.82	0.0524	103.15
4	0.0508	21.67	0.0520	102.36
5	0.0508	21.77	0.0523	102.95
6	0.0508	21.77	0.0523	102.95
7	0.0508	21.84	0.0524	103.15
8	0.0508	21.92	0.0526	103.54
				Av. 102.88

Comparison of Distillation Procedures

The standard procedure for the distillation of pentoses produces low results, which may be attributed to the destruc-

tion of the furfural by the acid upon long exposure. To overcome this difficulty Jolles (*3*) and Pervier and Gortner (*7*) have used steam distillation on xylose and arabinose and report practically complete recovery of the furfural based on the pentose used, whereas Kline and Acree (*4*) find that steam distillation does not improve the yield over that from the standard distillation when xylose was being determined. It has been shown by Youngburg (*11*) that various pentoses and pentosans give by all known methods of distillation from 50 to 100 per cent yields of furfural, so that the furfural yield is not an accurate measure of the pentosan content of vegetable materials.

Table II. Methods of Distillation Applied to Furfural

Series and Number	Theoretical Weight of Furfural in Distillate Sample	0.1 *N* $Na_2S_2O_3$	Furfural Found by Titration	Furfural Recovery
	Gram	*Cc.*	*Gram*	%
		STANDARD METHOD		
1A	0.0516	20.48	0.0491	95.16
B	0.0516	20.66	0.0496	96.12
C	0.0516	20.61	0.0495	95.93
D	0.0516	20.56	0.0493	95.54
E	0.0516	20.66	0.0496	96.12
2A	0.0496	20.77	0.0499	100.60
B	0.0496	20.63	0.0495	99.80
C	0.0496	20.75	0.0498	100.40
D	0.0496	20.67	0.0496	100.00
E	0.0496	20.60	0.0494	99.60
3A	0.0568	23.71	0.0569	100.18
B	0.0568	23.67	0.0568	100.00
C	0.0568	23.83	0.0572	100.70
D	0.0568	23.85	0.0572	100.70
E	0.0568	23.77	0.0571	100.53
4A	0.0504	20.65	0.0499	99.01
B	0.0504	20.63	0.0498	98.81
C	0.0504	20.67	0.0499	99.01
5A	0.0528	21.65	0.0523	99.05
B	0.0528	21.69	0.0524	99.24
C	0.0528	21.67	0.0523	99.05
			Av.	98.83
		STEAM DISTILLATION METHOD		
1A	0.0508	21.51	0.0516	101.58
B	0.0508	21.46	0.0515	101.48
C	0.0508	21.56	0.0518	101.97
D	0.0508	21.59	0.0518	101.97
E	0.0508	21.62	0.0519	102.17
2A	0.0507	21.62	0.0519	102.37
B	0.0507	21.69	0.0520	102.56
C	0.0507	21.73	0.0521	102.76
D	0.0507	21.79	0.0523	103.15
E	0.0507	21.73	0.0521	102.76
3A	0.0551	22.44	0.0542	98.37
B	0.0551	22.41	0.0541	98.19
C	0.0551	22.04	0.0542	98.37
4A	0.0546	23.09	0.0558	102.20
B	0.0546	23.14	0.0559	102.38
C	0.0546	23.21	0.0559	102.38
			Av.	101.54

Consequently, in order to contrast the procedures under comparable conditions, furfural samples were subjected to the two types of distillation and the recovery measured by the same method of analysis in both cases. Samples of about 5 grams of freshly distilled furfural were distilled by the A. O. A. C. method and the distillate was made up to 500 cc. from which 5-cc. aliquots were analyzed by the volumetric potassium bromate–bromide method. In all cases the solution being distilled turned dark and a brownish precipitate separated out as the distillation proceeded. Samples were also distilled from 12 per cent hydrochloric acid using the steam distillation method, in which a slow stream of steam was led into the distilling flask while it was maintained at 103° to 105° C. When no further test for furfural was obtained, the distillate was analyzed volumetrically. The results appearing in Table II (98.83 per cent recovery when ordinary distillation is employed and 101.54 per cent when steam distillation is used) indicate an average furfural recovery in the second method 2.71 per cent higher than in the first with 12 per cent hydrochloric acid alone. The greatest variations in furfural recovered by distilling pure furfural were 5.5 per cent with 12 per cent hydrochloric acid alone and 5 per cent with steam and 12 per cent hydrochloric acid.

Furfural Production from Hardwoods

Only a limited amount of data is available on the pentosan content or furfural yield of American hardwoods, the available data being the results of investigations carried on at the U. S. Forest Products Laboratory (*10*) by using the standard A. O. A. C. method of determination.

In the present work, samples of six species of air-dried wood were prepared by filing an entire cross section with a coarse wood rasp and the filings were used which would pass through a 40-mesh sieve but would be retained by an 80-mesh sieve. The moisture content of each sample was determined by drying it to constant weight at 105° C. and all results are based on the dried sample. One-gram samples were distilled by the 12 per cent hydrochloric acid–steam distillation method at a rate which produced slightly less than 500 cc. in 4 to 5 hours. At the end of this time no further test for furfural was obtained with aniline acetate.

The distillate, which was protected by passing it into the receiver through a small filter, was then made up to 500 cc., the acidity of the solution was determined, and sufficient concentrated hydrochloric acid was added to bring the concentration up to 12 per cent hydrochloric acid. The furfural content was then determined by the volumetric method by using 200-cc. aliquots and an accompanying check by the phloroglucinol precipitation method was run on a 300-cc. aliquot.

The results recorded in Table III show a close agreement between the two methods of determination, the volumetric being slightly higher here as in the determination of pure furfural. In the analysis of six woods the volumetric bromate-bromide titration gave from 0.2 to 0.86 per cent higher furfural yields than the phloroglucinol method, or a difference of 1.5 to 5.0 per cent of the furfural itself. The widest variations in several determinations of furfural from each of the six woods were, respectively, 2.3, 2.2, 1.5, 1.2, 0.77, and 2.3 per cent of the furfural by the bromate-bromide method, and with phloroglucinol they were approximately 3.7, 0.8, 4.4, and 2.4 per cent with four of these woods. In the precipitation method other compounds such as methyl furfural and hydroxymethyl furfural enter into reaction and are determined with the furfural. Undoubtedly these compounds may have an effect in the volumetric procedure, although this possible effect has not been determined.

Conclusions

The volumetric method of determination of furfural as proposed by Powell and Whittaker gave consistent results which compare favorably with the gravimetric methods with either phloroglucinol or thiobarbituric acid. The widest variations observed in the different methods of analyzing weighed portions of furfural were about 2 per cent with phloroglucinol, 1 per cent with thiobarbituric acid, and 1.2 per cent with potassium bromate–bromide. By the volumetric procedure the whole determination may be made in one day whereas the A. O. A. C. method requires a longer time.

The steam distillation of furfural from a 12 per cent hydrochloric acid solution led to a recovery which was 2.71 per cent higher than in the ordinary distillation with 12 per cent hydrochloric acid. This would indicate less destruction of the furfural during the time of distillation.

Six species of hardwoods have been distilled with steam and 12 per cent hydrochloric acid to yield furfural which has been determined volumetrically. This method gave

TABLE III. DETERMINATION BY VOLUMETRIC AND PHLOROGLUCINOL METHODS

	Volumetric Method				Phloroglucinol Method				
Sample	Weight	0.1 *N* $Na_2S_2O_3$	Weight of furfural	Furfural	Weight	Weight of precipitant	Weight of precipitate	Weight of furfural	Furfural
	Gram	*Cc.*	*Gram*	%	*Gram*	*Gram*	*Gram*	*Gram*	%
				YELLOW BIRCH—*Betula lutea*					
1A	0.1939	14.92	0.0358	18.46	....	....	....	....	...
B	0.1939	14.86	0.0358	18.46	....	....	....	....	...
C	0.1939	14.88	0.0357	18.41	....	....	....	....	...
2A	0.1936	14.85	0.0356	18.39	0.2904	0.3990	0.0948	0.0518	17.84
B	0.1936	14.72	0.0353	18.23	....	....	....	....	...
C	0.1936	14.79	0.0355	18.34	....	....	....	....	...
3A	0.1936	14.55	0.0349	18.03	0.2904	0.4002	0.0910	0.0499	17.18
B	0.1936	14.58	0.0350	18.08	....	....	....	....	...
C	0.1936	14.58	0.0350	18.08	....	....	....	....	...
				Av. 18.27					Av. 17.51
				PAPER BIRCH—*Betula papyrifera*					
1A	0.1917	15.23	0.0365	19.04	0.2875	0.4003	0.0956	0.0523	18.19
B	0.1917	15.17	0.0364	18.99	....	....	....	....	...
C	0.1917	15.20	0.0365	19.04	....	....	....	....	...
2A	0.1917	15.05	0.0361	18.83	....	....	....	....	...
B	0.1917	15.00	0.0360	18.78	....	....	....	....	...
C	0.1917	15.03	0.0361	18.83	....	....	....	....	...
3A	0.1917	14.88	0.0357	18.62	0.1917	0.4000	0.0615	0.0346	18.05
B	0.1917	14.93	0.0358	18.67	....	....	....	....	...
C	0.1917	14.92	0.0358	18.67	....	....	....	....	...
				Av. 18.83					Av. 18.12
				SUGAR MAPLE—*Acer saccharum*					
1A	0.1911	11.51	0.0276	14.44	....	....	....	....	...
B	0.1911	11.48	0.0276	14.44	....	....	....	....	...
C	0.1911	11.51	0.0276	14.44	....	....	....	....	...
2A	0.1910	11.68	0.0280	14.66	....	....	....	....	...
B	0.1910	11.70	0.0280	14.66	....	....	....	....	...
C	0.1910	11.68	0.0280	14.66	....	....	....	....	...
3A	0.1912	11.52	0.0276	14.44	....	....	....	....	...
B	0.1912	11.50	0.0276	14.44	....	....	....	....	...
C	0.1912	11.55	0.0277	14.49	....	....	....	....	...
4A	0.1911	11.54	0.0277	14.50	0.2867	0.4004	0.0703	0.0391	13.64
B	0.1911	11.49	0.0276	14.44	....	....	....	....	...
C	0.1911	11.51	0.0276	14.44	....	....	....	....	...
				Av. 14.50					
				WHITE ASH—*Fraxinus americana*					
1A	0.1924	11.15	0.0268	13.93	....	....	....	....	...
B	0.1924	11.16	0.0268	13.93	0.2886	0.4003	0.0698	0.0389	13.48
C	0.1924	11.14	0.0267	13.86	....	....	....	....	...
2A	0.1925	11.30	0.0271	14.08	....	....	....	....	...
B	0.1925	11.35	0.0272	14.13	0.2888	0.4010	0.0733	0.0407	14.09
C	0.1925	11.33	0.0272	14.13	....	....	....	....	...
3A	0.1923	11.21	0.0269	13.99	....	....	....	....	...
B	0.1923	11.25	0.0270	14.04	0.2885	0.3998	0.0719	0.0400	13.87
C	0.1923	11.26	0.0270	14.04	....	....	....	....	...
				Av. 14.01					Av. 13.81
				NORTHERN RED OAK—*Quercus borealis*					
1A	0.1889	12.10	0.0290	15.35	....	....	....	....	...
B	0.1889	12.11	0.0291	15.40	0.2834	0.4005	0.0744	0.0413	14.57
C	0.1889	12.09	0.0290	15.35	....	....	....	....	...
2A	0.1891	12.06	0.0289	15.28	....	....	....	....	...
B	0.1891	12.11	0.0291	15.39	0.2837	0.4011	0.0756	0.0419	14.77
C	0.1891	12.08	0.0290	15.34	....	....	....	....	...
3A	0.1889	12.03	0.0289	15.30	....	....	....	....	...
B	0.1889	12.11	0.0291	15.40	0.2834	0.4001	0.0764	0.0423	14.93
C	0.1889	12.08	0.0290	15.35	....	....	....	....	...
				Av. 15.35					Av. 14.76
				BEECH—*Fagus grandifolia*					
1A	0.1928	12.86	0.0309	16.03	....	....	....	....	...
B	0.1928	12.89	0.0309	16.03	....	....	....	....	...
2A	0.1928	12.67	0.0304	15.77	....	....	....	....	...
B	0.1928	12.62	0.0302	15.66	....	....	....	....	...
C	0.1928	12.67	0.0304	15.77	....	....	....	....	...
3A	0.1932	12.75	0.0306	15.84	....	....	....	....	...
B	0.1932	12.72	0.0305	15.79	....	....	....	....	...
C	0.1932	12.77	0.0306	15.84	....	....	....	....	...
4A	0.1928	12.69	0.0305	15.82	0.2892	0.4006	0.0811	0.0447	15.47
B	0.1928	12.77	0.0306	15.87	....	....	....	....	...
C	0.1928	12.76	0.0306	15.87	....	....	....	....	...
				Av. 15.84					

results which were 0.2 to 0.86 per cent higher than by the phloroglucinol method or a difference of 1.5 to 5.0 per cent of the furfural itself. The widest variations in several determinations of furfural from each of the six woods were, respectively, 2.3, 2.2, 1.5, 1.2, 0.77, and 2.3 per cent of the furfural by the bromate-bromide method, and with phloroglucinol they were approximately 3.7, 0.8, 4.4, and 2.4 per cent with four of these woods.

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Interference of Pyridine Derivatives in Arsenic Determination

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Low results for arsenic are obtained in analyzing tobacco by the Gutzeit method after acid digestion. These low results are caused by undigested residues of nicotine, which retard the evolution of hydrogen and arsine during analysis. Every other pyridine derivative tested, as well as pyridine itself, behaves similarly. Data are offered to show the quantitative nature of the interference produced by the pyridine compounds studied. A procedure is given for eliminating such interference so that correct results can be obtained by the Gutzeit method.

Organic products of plant or animal origin are usually analyzed for arsenic by the Gutzeit method, the material first being digested with nitric and sulfuric acids in order completely to oxidize the organic matter and place the arsenic in solution. Except for a few minor differences, which do not affect the final results, this laboratory employs the technic of the Association of Official Agricultural Chemists (*1*). This method gives very low yields when used for the determination of arsenic in tobacco. In most cases of routine analysis, the recoveries amount to only 60 to 95 per cent of the arsenic present, and in extreme cases they may be less than 50 per cent.

Nicotine Interference

Abnormal conditions of hydrogen evolution caused by undigested organic residues of the tobacco alkaloid nicotine were identified as being responsible for the low results encountered. These abnormal conditions, and their effects on the results of analysis, may be described as follows:

1. As the evolution of hydrogen proceeds, the solutions become darkened by a very fine suspension of tin originating from the stannous chloride reagent. Apparently none of the tin adheres to the zinc. Under normal conditions, the tin coats the zinc and forms gray flocculent masses, which finally drift to the surface, leaving the solution clear. In the present case, the failure of the tin to adhere to and properly sensitize the zinc accounts, at least in part, for the retarded rate of evolution described next.

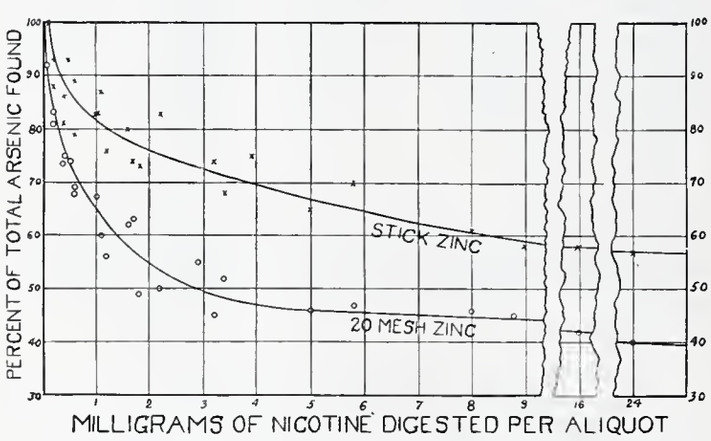

Figure 1. Effect of Nicotine on Determination of Arsenic by Acid Digestion and Gutzeit Method

2. The presence of undigested nicotine residues slows down the rate of evolution of hydrogen to a marked degree. Those familiar with the Gutzeit method will at once recognize that this condition is certain to lead to low results of analysis. It is a well-known fact that stains formed by a given amount of arsine under conditions of slow or retarded evolution of hydrogen are deposited over a shorter length of strip than when the evolution conditions are normal. It follows that the stains formed under conditions of retarded evolution will be under-evaluated when they are compared with the standard stains of known value during the course of a normal evolution.

3. The arsenic is not completely converted to arsine during the usual period of evolution (1.5 hours). Appreciable stains result when the evolution is continued for an additional period after fresh acid, zinc, and mercuric bromide strips have been added.

Interference of Pyridine Compounds in General

The nicotine molecule is composed of a pyridine ring combined with an *N*-methylpyrrolidine ring. The author's investigations showed that the pyridine ring of the molecule is the specific cause of the low results. The following experiment was made in demonstrating this point:

Separate acid digestions were made of pure samples of nicotine, pyridine, and *N*-methylpyrrolidine, to which had been added known amounts of arsenic. The existence of undigested organic residues could be demonstrated in all these solutions by the charring which took place when individual portions were evaporated to dryness and ignited.

Analyses by the Gutzeit method showed that the presence of *N*-methylpyrrolidine residues interfered in no way with the results of analysis, but that nicotine and pyridine residues caused the same abnormal conditions to appear during analysis and the same condition of low results that had been encountered in analyzing tobacco. Subsequently, a number of pyridine derivatives were tested, and all acted in a similar manner. It should therefore be noted that interference of this sort is not necessarily confined to tobacco, but can be expected during the analysis of any product containing pyridine or its derivatives.

Methods for Eliminating Interference

Interference caused by pyridine residues can be eliminated by dry-ashing the digested solution. This method is not convenient, however, because of the difficulties connected with disposing of the large amounts of sulfuric acid evaporated.

The most convenient method developed to eliminate the interfering compounds makes use of the A. O. A. C. procedure (*2*) for the treatment of coal-tar food colors preliminary to analysis by the Gutzeit method. By means of this method, the arsenic is precipitated along with the phosphate by treatment of the digested solution with ammonium hydroxide,

phosphoric acid, and magnesia mixture. The precipitate containing the arsenic can then be filtered and washed free of the soluble pyridine residues, redissolved in a hydrochloric acid solution, and analyzed by the Gutzeit method.

The method, as modified and simplified for use in analyzing tobacco, may be described as follows:

Reagents. All reagents should be arsenic-free.

Ammonium hydroxide, containing not less than 26 per cent by weight of NH_3.

Dilute ammonium hydroxide (1 to 9).

Dilute phosphoric acid, 19 cc. of H_3PO_4, 85 per cent, diluted to one liter.

Magnesia mixture, containing 55 grams of hydrated magnesium chloride, 55 grams of ammonium chloride, and 88 cc. of ammonium hydroxide per liter.

Dilute hydrochloric acid (1 to 4).

Procedure. Make an acid digestion of a suitable sample in the usual manner. Transfer an aliquot of the diluted digested solution representing about 0.2 mg. of arsenic trioxide to a 400-cc. beaker. (In the absence of a rough idea regarding the amount of arsenic contained by the sample, the size of this aliquot must be determined by trial.) Dilute to 150 to 200 cc. Make alkaline with ammonium hydroxide, add 20 cc. of the dilute phosphoric acid, and then slowly add 25 cc. of the magnesia mixture, stirring meanwhile. Add 5 cc. of c. p. ammonium hydroxide, stir, and then allow the mixture to stand for at least 15 minutes. Filter through an 11-cm. paper, and rinse the precipitate with several 15-cc. portions of the dilute ammonium hydroxide and finally with 10 cc. of water. Drain for at least 15 minutes, occasionally tamping the glass funnel against the funnel support to settle the precipitate and encourage the drainage of the last few cubic centimeters of filtrate. Dissolve the precipitate in 40 cc. of the dilute hydrochloric acid, pouring the acid on the filter in small portions and allowing it to drain into a 100-cc. volumetric flask. Rinse the filter in the same way with about 50 cc. of water and dilute the solution to volume. Use 5- to 20-cc. aliquots for the Gutzeit analysis. Add to the acid in the aliquot sufficient c. p. concentrated hydrochloric acid to make its total volume 5 cc. Complete the determination as directed in the A. O. A. C. method (*3*), beginning with "Add 5 cc. of the KI reagent."

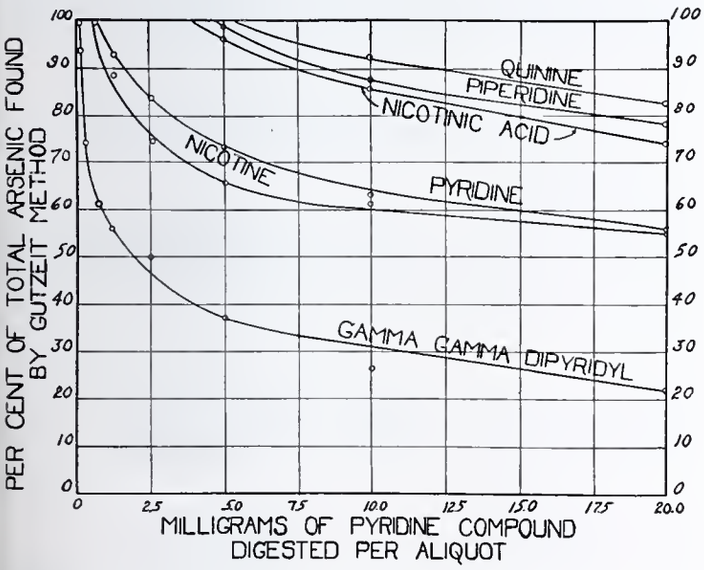

Figure 2. Arsenic Recovered in Presence of Pyridine Compounds, Using 20-Mesh Zinc for Hydrogen Generation

Quantitative Interference of Nicotine

Analyses were made to determine the extent to which the amounts of nicotine normally present in tobacco had lowered the results of analysis. The method of analysis described above was used for comparison. Eight samples of powdered dry tobacco leaves which carried arsenical residues ranging from the heaviest to the lightest encountered in routine analysis were selected for analysis. One portion of each sample was analyzed for nicotine, while a second portion was digested in the usual manner for arsenic analysis. The digested solutions were diluted until 5- to 15-cc. aliquots of each contained arsenic ranging from about 0.010 to 0.040 mg. of arsenic trioxide. Each digested solution was analyzed by the Gutzeit method both before and after phosphate precipitation. Since the A. O. A. C. method permits the use of either granulated or stick zinc, a complete set of analyses as described above was made with each type of zinc. The results before precipitation were then calculated as percentages of the amounts found after precipitation.

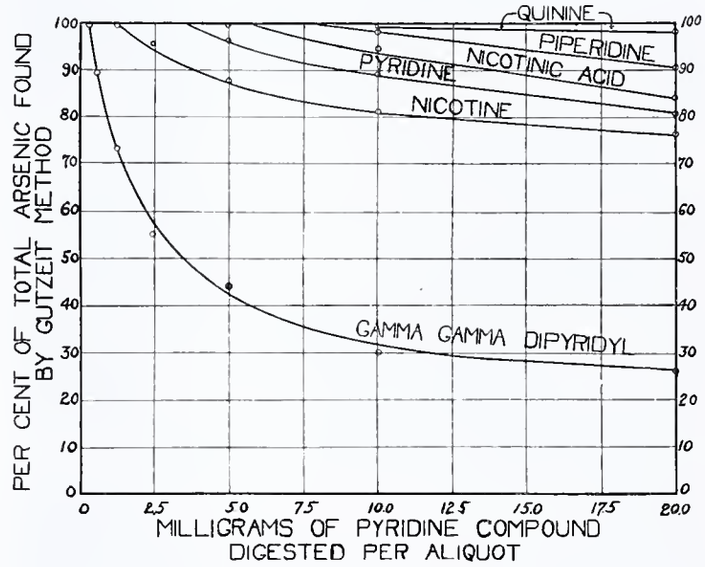

Figure 3. Arsenic Recovered in Presence of Pyridine Compounds, Using Stick Zinc for Hydrogen Generation

The relation between the yields of arsenic and the amounts of nicotine represented by the aliquot is shown in Figure 1. Although individual observations are somewhat scattered, the composite curves indicate that a distinct correlation exists. It is observed also that the recoveries obtained with stick zinc are distinctly superior to those with 20-mesh zinc. The reason for this was not discovered, but the circumstance should not be interpreted as meaning that stick zinc is consequently to be preferred for general purposes of analysis. Our tests with these two forms of zinc show that under normal conditions they give results of practically equal accuracy.

Quantitative Interference Produced by Different Pyridine Compounds

In view of the fact that pyridine or its derivatives may be present in products other than tobacco which are assigned to the chemist for arsenic analysis, it is of interest to know to what degree different pyridine compounds interfere with the results of analysis by the Gutzeit method. With this end in view, the following pyridine compounds were made the subjects of experiment:

Pyridine	C_5H_5N
Nicotinic acid	$C_5H_4N\ COOH$
γ-γ-Dipyridyl	$(C_5H_4N)_2$
Piperidine	$C_5H_{11}N$
Nicotine	$C_{10}H_{14}N_2$
Quinine	$C_{20}H_{24}O_2N_2$

Procedure. Two grams of each compound were thoroughly digested with nitric and sulfuric acids to as nearly a colorless solution as could be produced. Each digested solution was diluted to one liter after sufficient standard arsenic pentoxide solution had been added to make the diluted solution contain the equivalent of 2 micrograms of arsenic trioxide per cubic centimeter. This solution was designated in each case as solution 1. Thereafter, solutions 2, 3, 4, etc., were prepared from a portion of each preceding solution in such a way that each contained the same concentration of arsenic and of sulfuric acid, but one-half as much of the digested pyridine compound as had been contained in the preceding solution.

Solutions 1, 2, 3, etc., of each digested compound were then analyzed by the Gutzeit method until a dilution was reached which caused no visible interference with the results of analysis. In each case, 5-, 10-, and 15-cc. aliquots, corresponding to 10, 20, and 30 micrograms of arsenic trioxide, were used. One set of analyses was made with stick zinc, and a second set was made with granulated zinc (20-mesh) at the rate of 2 grams per generator bottle. The results of analysis were calculated as percentage recovery of the total amount of arsenic present.

The data showed that the percentage of arsenic recovered depends solely on the amount of interfering compound present, and is not influenced by the amount of arsenic contained by the aliquot, at least not through the range of 10 to 30 micrograms.

Figure 2 shows the average percentage of the total arsenic recovered in the presence of pyridine compounds ranging from 0 to 20 mg. digested per aliquot used. Granulated zinc (20-mesh) at the rate of 2 grams per generator bottle was used in these analyses.

It will be observed that γ-γ-dipyridyl exerts a tremendous degree of depression on the results of analysis, and that nicotine and pyridine produce a marked depression; whereas nicotinic acid, piperidine, and quinine cause much less interference. It would not be expected that quinine would have a great restraining influence, inasmuch as its one pyridine ring is only a small part of its total molecular structure.

Figure 3 is based upon the results of analyses similar to those used for Figure 2, except that stick zinc was used for evolution purposes. It will be noted that with the exception of γ-γ-dipyridyl the results of analysis are distinctly higher when stick zinc instead of granular zinc is used. This same circumstance was noted previously in connection with the tobacco analyses shown in Figure 1.

A comparison of the nicotine curves in Figures 1, 2, and 3 shows that much lower results were caused by nicotine during routine tobacco analysis than when the digestions were made with pure nicotine. This would indicate that the method of nicotine analysis does not detect all the interfering compounds present in tobacco.

It may be mentioned here that the ability of pyridine compounds to cause these disturbed evolution conditions does not originate as a result of digestion with nitric and sulfuric acids. The pyridine compounds before digestion cause the same type of interference to an equal or a greater degree than they do after digestion.

General Considerations

Aside from tobacco, not many products which are analyzed for arsenic are likely to contain pyridine or its derivatives in amounts sufficient to cause low results of analysis. Among the possibilities are materials containing animal hides, bones, or bone oil.

It is possible also that apples sprayed late in the season with nicotine sulfate may contain nicotine residues sufficient to interfere with the determination of arsenical residues deposited during previous sprayings with lead arsenate.

Unsuspected sources of pyridine interference may likewise be encountered at times in organic products of unknown origin or composition. When materials of this nature are being analyzed for arsenic, it would be advisable to observe closely the character of the evolution and, in case of any abnormal appearance, to verify the results by making analyses after phosphate precipitation.

Acknowledgment

The author wishes to express his appreciation for the assistance rendered by Julian Hiley in carrying on much of the analytical work connected with this investigation.

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Analysis of White Metals and Their Smelter Products

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THE samples as delivered from the sample mill consist mostly of a bar and slag which have to be weighed out in proportional parts. The metallic part, however, is generally not uniform, so that a larger sample has to be taken in order to get a good average. This difficulty obviously does not exist in the case of slags which are perfectly well miscible.

The method of analysis as used in the laboratory of the U. S. Metals Refining Company begins differently from the methods generally used, which consist in a separation of the tin from the rest of the other metals by precipitating it as metastannic acid in nitric acid solution. This method of attacking the white metals with nitric acid has the undeniable disadvantage that the metastannic acid is never chemically pure, that a small part of the tin goes into solution, and that a very difficult operation ensues as soon as a greater weight of metal is taken for analysis.

Therefore, experience has shown that it is preferable in any case to dissolve the metallic part to a clear solution in hydrochloric acid, and take this solution as the starting point for further operation. The antimony and copper, which are attacked with difficulty by hydrochloric acid, are dissolved by an addition of sodium chlorate dissolved in water, or by a few drops of nitric acid. The oxidizing substance is chosen according to a preliminary test for copper. If this test shows that the copper is low, then the antimony and copper are oxidized with sodium chlorate so that a straight volumetric determination can be made later.

The method used for the bar is as follows: The proportional part corresponding to 20 grams of the sample is dissolved in a 500-cc. flask with concentrated hydrochloric acid at moderate heat. After the reaction ceases, the antimony and copper are dissolved by adding just enough oxidizing agent for the purpose. The flask is then cooled and filled up to the mark with concentrated hydrochloric acid, the contents are mixed, and the flask held in readiness for the slag part.

If it is intended to run the tin by the straight volumetric

method, it has to be attacked only by concentrated hydrochloric acid plus water at boiling temperature, using sodium chlorate to dissolve the antimony. For the determination of lead, copper, and antimony, any suitable acid may be used. If the slag does not dissolve, it has to be fused with sodium peroxide and treated according to the following procedure:

TIN. One-half gram is weighed into a nickel crucible, fused with sodium peroxide, and the fusion decomposed with water in a 400-cc. beaker. To this fusion 12.5 cc., equal to 0.5 gram, are tapped from the 500-cc. flask. If a preliminary test shows the absence of copper in great quantities, the solution is neutralized with hydrochloric acid, and an excess of 80 cc. is added. This solution, which should be about 200 cc., is boiled for a few minutes to expel all chlorine, and is then ready to be reduced and titrated according to standard methods.

If the preliminary test shows high copper, the procedure is somewhat different. To the clear solution of hydrochloric acid are added 10 to 15 cc. of ferric chloride solutions (500 grams of ferric chloride to 5000 cc. of water), then ammonium hydroxide in excess, and 3 to 5 grams of ammonium carbonate. This is boiled for a short time and filtered. After the copper is washed out, a hole is punched in the filter paper through which the precipitate is washed into a 500-cc. Erlenmeyer flask. The adhering precipitate is cleaned from the filter paper by washing out with hydrochloric acid (1 to 1). (It is not necessary to wash out the copper quantitatively from the precipitate of the hydroxides, as copper in small quantities does not influence the titration of the tin.) Enough hydrochloric acid is then added to the solution to bring the total free acid up to 80 cc. It is then ready to be run for tin according to standard methods.

LEAD AND COPPER. If the slag does not dissolve in acid, one gram of it is fused in an iron crucible with sodium peroxide. The fusion is decomposed with water in a 600-cc. beaker, 25 cc. (equal to one gram) are tapped from the solution of the metallic part, and 60 to 70 cc. of yellow sodium sulfide (2500 grams of sulfide crystals dissolved in 12 liters of water with enough sulfur added to make the solution deep yellow) added to separate the lead and copper from the tin and antimony. The solution is boiled moderately, filtered, and washed twice with sodium sulfide containing hot water. Then the filter paper plus the precipitate is brought back to the beaker, 25 cc. of concentrated sulfuric acid added, and the paper destroyed by addition of nitric acid. After strong fuming, water is added and the solution boiled until the ferric salts dissolve.

The lead sulfate is separated from the solution by filtration, and the lead determined as chromate according to standard methods.

In the filtrate the copper is determined according to the potassium sulfocyanate method with subsequent electrolysis.

ANTIMONY. Two grams of the slag are fused in an iron crucible. The fusion is decomposed with water, 50 cc. (equal to 2 grams) of the solution of the metallic part are added, and the alkaline solution saturated with 70 to 80 cc. of yellow sodium sulfide. This solution is transferred to a 500-cc. flask and, after cooling, 250 cc. (equal to one gram) are filtered through dry filter paper. These 250 cc. are acidified with 100 cc. of concentrated hydrochloric acid, the solution boiled down to 150 to 175 cc., then 30 cc. of concentrated hydrochloric acid added and the solution gassed for 20 to 30 minutes with hydrogen sulfide to remove the arsenic as arsenous sulfide. The subsequent filtration is best done through a filter paper which has previously been moistened with hydrochloric acid (1 to 1). After two washings with this hydrochloric acid, the filter is finally washed with hot water. To this filtrate 3 to 5 grams of sodium chlorate are added and the solution boiled down to crystals. After cooling, 100 cc. of water are added and the solution shaken until it is clear. Then a few crystals of potassium iodide are added and the liberated iodine titrated with sodium thiosulfate.

NOTES. If the lead content of the white metal products becomes very high, the solution has to be made in a 1000-cc. flask in order to keep the lead chloride from precipitating in the hydrochloric acid solution. In adding the oxidizing reagent, an excess of nitric acid must be avoided. If too much acid has been added and the lead chloride crystals begin to precipitate after cooling, the whole solution plus the precipitated lead chloride must be transferred to a bigger flask so that the greater quantity of hydrochloric acid can keep the lead chloride in solution.

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Modified Combustion Apparatus

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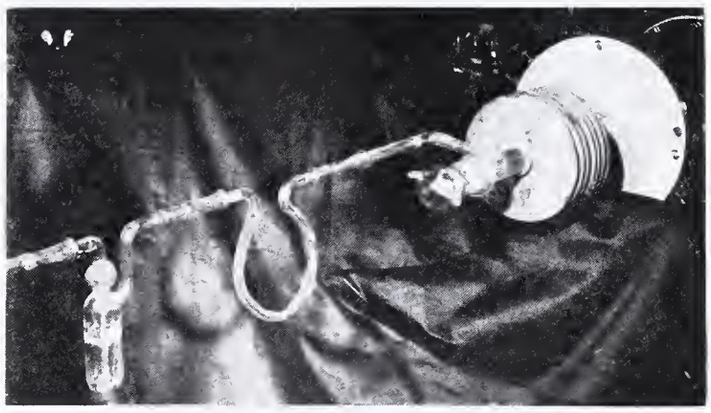
SEVERAL improvements in analytical combustion apparatus have been recently published (*1, 3*), one of which is the use of interchangeable ground-glass joints (*2*). The chief difficulties in the latter design are the faulty alignment of the individual units which go to make up the train, the liquefaction of the grease on the ground joints of the combustion tube, and the delay and awkwardness in the process of inserting the boat containing the sample to be analyzed.

The photograph illustrates the manner in which these difficulties were overcome in this laboratory. A circular flexible piece of glass tubing in the train allowed for expansion on heating and also compensated for lack of alignment. The side arm of the combustion tube made it possible to insert the sample without interrupting the flow of gas or without dis-



connecting the sections of the train. Finally, copper radiating vanes were fitted to the quartz tube by first winding the tube with fine copper wire and then soldering the copper collar, with the attached radiating fins, to the layer of copper wire. Ordinary stopcock grease was used with no difficulty when the joints were protected from the thermal flow in this manner.

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Steam vs. Ether in Separation of Acids from Bacteriological Media

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THE experiments outlined in this paper were carried out to show the great inefficiency in the estimation of organic acids separated from bacteriological media by the customary steam distillation, that this separation may be done much better by ether, and that the time and tediousness of the operation are much less when ether is used.

For more than twenty years it has been customary in some laboratories to obtain the volatile acids from bacteriological media by steam distillation. The medium is acidified with sulfuric or phosphoric acid. This distillate is neutralized with sodium or barium hydroxides and concentrated by evaporation. The concentrate is subjected frequently to analysis for acids according to the method of Duclaux (*9*).

The nonvolatile (fixed) acids are considered as remaining in the residue in the distillation flask, from which they are obtained by extraction with ether. In order to determine the amount of acids produced by the bacteria, an aliquot of uninoculated media is subjected to the same analysis as an inoculated portion and the difference in acidity between the inoculated and uninoculated media is taken as the acidity produced by bacteria.

Methods similar to the foregoing have been used by Harden (*14*), Selieber (*19*), Fred and Peterson (*12*), Zoller and Clark (*6*), and others, in determining the acids produced by bacteria; by Jensen (*15*) in studying the volatile aliphatic acids of Swiss cheese; by Freudenreich and Jensen (*13*) in their researches in Emmenthaler cheese; by Currie (*7*) in his investigation of Roquefort cheese; by Susuki, Hastings, and Hart (*20*) in their studies on the acids of Cheddar cheese; by Richmond (*18*) and Edelstein and Csonka (*10*) in determining the acids formed by decomposition in milk; by Dox and Neidig (*8*) in their work on the volatile aliphatic acids of corn silage; by Woodman and Burwell (*21*) in the detection of formic acid as a food preservative, and by many investigators of the acids of wine.

Errors in Old Method by Heat

pH Decrease in Heating Media. The importance of the effect of heat on the production of acid in bacteriological media has not been sufficiently emphasized in connection with the separation of acids by steam distillation. It has been noticed by workers in this subject that under the influence of heat bacteriological media tend to become more acid in reaction. Anthony and Ekroth (*2*) found that "the point at which no further acidity is produced was not reached with meat infusion (which had been previously subjected to boiling over the open flame for one to two hours) even after prolonged autoclaving at 15 pounds pressure for eight hours." Clark (*6*) found that a meat infusion containing 0.5 per cent potassium monophosphate, brought to a reaction of pH 7.19 before sterilization, changes to pH 6.70 after sterilization.

McIntosh and Smart (*16*) confined their observations to the effect of the maximum amount of heat employed, under ordinary conditions, to sterilize the media. Broth subjected to three steamings of 20 minutes each caused a decrease in pH of 0.13; after the same number of autoclavings at 115° C. for 20 minutes, the figure was 0.23. In the case of 1 per cent glucose broth, the reaction decreased as much as pH 1.2 during autoclaving.

It is obvious that the increase in acidity which takes place during sterilization can also continue during the hours of steam distillation.

Acid Increase in Heating Sugars with Amino Acids. Mudge (*17*) maintains that it is the presence of an unstable sugar molecule together with an amino acid which gives rise to part of the acidity of sterilization. He bases this conclusion on experiments with a 0.5 per cent solution of alanine, and to a 1 per cent solution of maltose or raffinose. Solutions were also used which contained 0.5 per cent of alanine and 1 per cent of the sugars mentioned. These solutions were sterilized in the autoclave for periods of 15 minutes, 30 minutes, and 1 hour. All of the solutions were neutral to phenolphthalein at the start. The results show that alanine alone and sugar alone give no acidity; a mixture of alanine and raffinose remains neutral even after heating for an hour; but a solution containing a mixture of alanine and maltose becomes acid, presumably according to the equation:

$$H_3C—CH—NH_2—COOH + H_2C{:}O = H_3C—CH—NCH_2—COOH + H_2O$$

Acid Increase in Heating Sugars with Mineral Acids. It is evident, however, that this is not the only possible source of acidity. The prolonged action of mineral acids upon glucose, accelerated by heat, results in the well-known cleavage of glucose into levulinic and formic acids. To prove this, the following experiment was performed:

One and one-fourth grams of c. p. dextrose were dissolved in 250 cc. distilled water; 1.6 cc. of 25 per cent H_3PO_4 were added. This was steam-distilled. The first 500 cc. of distillate contained 0.4 cc. of 0.1 *N* acid; the second, 0.25 cc.; the third and fourth, 0.65 cc.; the fifth was lost; the sixth, 0.30 cc.; the seventh, 0.25 cc.; the eighth, 0.30 cc.; the washings from condenser, 0.15 cc.; total, 2.30 cc. of 0.1 *N* acid. This distillate was evaporated on the steam bath to about 100 cc. and then treated with the mercuric chloride–formic acid reagent (for details of formic estimation, see the official method, *3*). As a result, 0.0232 gram of mercurous chloride was obtained, equivalent to 2.03 cc. of 0.1 *N* formic acid.

Molecular Changes among Organic Acids. Besides the changes in acidity caused by the possible decomposition of proteins, fats, and carbohydrates, there is the probable change in the structure of the acids themselves. Erlenmeyer (*1*) found that formic acid is formed by heating lactic acid with dilute sulfuric acid. To demonstrate this reaction under the usual conditions of media distillation, the following experiment was carried out:

Three cubic centimeters of 25 per cent H_3PO_4 (U. S. P.) and 86.65 cc. of 0.1 *N* barium lactate were diluted to 250 cc. with distilled water. The reaction of the mixture was then blue to Congo red, and brown to thymol blue. This liquid was steam-distilled under constant volume. The first liter of distillate contained 2.4 cc. of 0.1 *N* acid; the second, 2.1 cc.; the third, 1.9 cc.; total, 6.4 cc. of 0.1 *N* acid. The distillate was evaporated on the steam bath and treated with the mercuric chloride–formic acid reagent (*3*). As a result, 0.0046 gram of mercurous chloride was obtained, equivalent to 0.51 cc. of 0.1 *N* formic acid. As precautions were taken against carbon dioxide, the remainder of the acidity of the distillate (5.89 cc. of 0.1 *N*) was caused by lactic acid.

From the foregoing evidence it is clear that, during the steam distillation of bacteriological media practiced for the recovery of volatile acids and their separation from nonvolatile acids, an increased amount of acid as well as molecular change among the acids themselves is liable to occur. This is especially true if the steam distillation lasts for 10 hours, as is sometimes necessary.

Failure to Secure Comparable Data. It is likewise evident that, at the time distillation is begun, the inoculated and the uninoculated media do not have the same amounts or varieties of the various constituents. For instance, carbon dioxide may have been formed and partly escaped, or various acids may have been formed, or the sugar may have been partially decomposed in the inoculated media. Therefore, when both the inoculated and uninoculated media are subjected to distillation, they are not comparative and the effect of heat may differ in the production of the various acids involved.

Errors in Old Method Caused by Incomplete Separation of Acids

As has been shown above, a considerable amount of lactic acid may be carried over in the distillate during steam distillation.

The following experiments show that at least 25 per cent of the volatile acids may remain behind in the distillation flask unless the flask contents is sufficiently acidified with 25 per cent H_3PO_4, or by other adequate means previous to distillation.

A mixture of 9.69 cc. of 0.1 *N* formic, 9.365 cc. of 0.1 *N* acetic, 10.08 cc. of 0.1 *N* propionic, 9.744 cc. of 0.1 *N* lactic, and 10.00 cc. of 0.1 *N* succinic acids was diluted to 150 cc. with distilled water. The mixture therefore contained a total of 48.874 cc. of 0.1 *N* acid, of which 19.744 cc. were nonvolatile and 29.13 cc. volatile. When this was subjected to steam distillation and the volume kept constant, the first liter of distillate contained 21.78 cc. of 0.1 *N* acid; the second and third liter, 0.05 cc.; total, 21.785 cc. of 0.1 *N* acid. As there were 29.13 cc. of volatile acid in the distilling flask, from which only 21.78 cc. distilled, 7.35 cc. or 25.22 per cent of the volatile acid remained undistilled.

In a duplicate experiment in which the same acids in similar amounts were used, the first liter of distillate contained 20.97 cc. of 0.1 *N* acid; the second and third, 0.1 cc.; and the fourth, 0.1 cc. As only 20.97 cc. of 0.1 *N* acid out of 29.13 cc. of 0.1 *N* volatile acid distilled, 8.16 cc. or 28 per cent remained undistilled.

Error in Old Method in Concentrating Distillate

Loss of Acidity. In order to determine the amounts and varieties of the various acids present in the distillate, it is common practice to neutralize and concentrate the distillate by evaporation on a steam bath. In this process a loss of acidity is generally experienced and has frequently been mentioned (*11*).

A medium of meat infusion, 1.0 per cent Difco peptone, 2 per cent dextrose, and 1 per cent potassium monophosphate was made up to 250 cc., including 6 cc. of 25 per cent H_3PO_4 to make the liquid acid to Congo red. This was steam-distilled until the last 500 cc. of distillate contained only 0.8 cc. of 0.1 *N* acid. The total distillate contained 44.60 cc. of 0.1 *N* acid. This was evaporated on a steam bath to about 50 cc. The liquid after evaporation contained 39.66 cc. of 0.1 *N* acid or only 88.94 per cent of the original acidity of the distillate. A duplicate experiment resulted in 43.20 cc. of 0.1 *N* acid in the distillate, from which 40.12 cc. or 92.96 per cent remained after evaporation.

This loss is greater when evaporation is continued to dryness. Part of it may be due to decomposition by heat, as observed by Browne (*5*). There is also a loss of acid by evaporation, for the salts of the weak organic acids are appreciably hydrolyzed, and an odor of the acids can readily be detected above a hot solution neutral to phenolphthalein. The spontaneous decomposition of calcium butyrate at room temperature is shown by an odor of butyric acid from a bottle containing the salt.

To determine the loss of formic acid during evaporation, two portions of approximately 0.2 gram of calcium formate were dissolved in 300 cc. distilled water; 150 cc. of each of these solutions were tested for formic acid by the mercuric chloride reagent (*3*). The first portion contained 0.08231 gram (1.765 cc. of 0.1 *N*); the second portion, 0.09094 gram (1.929 cc. of 0.1 *N*) of formic acid. One hundred fifty cubic centimeters of each of the solutions were evaporated in 26.5-cm. porcelain evaporation dishes on a steam bath. Three liters of water were gradually added to each, and the evaporation continued almost to dryness. As a result, the first portion contained 0.08056 gram (1.709 cc. of 0.1 *N*) and the second portion contained 0.08899 gram (1.887 cc. of 0.1 *N*) of formic acid by the mercuric chloride method. There were, therefore, losses of 0.00175 gram or 2.14 per cent, and 0.00195 gram or 2.16 per cent during evaporation. (In concentrations of formic acid of less than 0.5 gram per liter, the average error is ±0.0005 gram or ±0.2 per cent for the mercuric chloride method.)

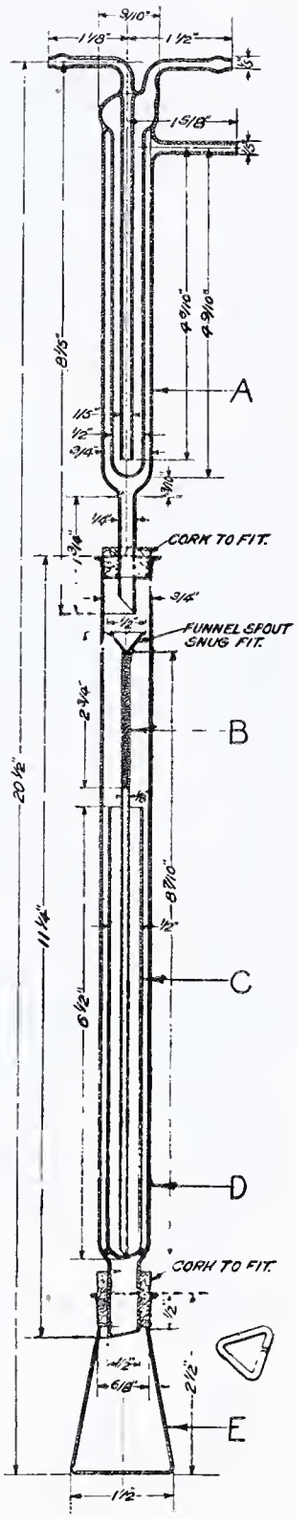

Figure 1. Ether Extraction Apparatus

Extraction of Acids by Ether

From evidence presented above, it is desirable to find a method for the separation of acids from bacteriological media which will eliminate the effects of heat on the media.

This is successfully carried out in the ethereal extraction of the nonvolatile acids from the distillation residue in the old method. Harden (*14*) in 1900 was able to remove completely lactic and succinic acids by continuous extraction in 10 hours. It was demonstrated as long ago as 1872 by Berthelot and Jungfleisch (*4*) that formic, acetic, butyric, and succinic acids may be extracted from aqueous solutions by shaking with ether. It was thought therefore that the extraction of all of the aliphatic acids met with in bacteriological media might be extracted with ether.

Extraction Apparatus. An ether extraction apparatus similar to Figure 1 was used in the following experiments.

A is the condenser, *D* the extraction tube, *C* the inner tube to hold the material to be extracted, *E* the flask for boiling the ether and also to retain the extract. In the apparatus illustrated, the inner tube is able to hold 100 cc. of media and have about 4 inches (10.2 cm.) of tube above. It is necessary to have considerable space above the medium in the inner tube in order to allow complete separation of the medium and ether. This is to prevent the overflowing of the medium to *E*. The distance between the top of the funnel and the top of the medium must be great enough to allow the ether to flow out of the bottom of the funnel stem. This distance increases with an increase in the specific gravity of the medium.

Extraction of Formic and Acetic Acids. To test the efficiency of the apparatus to extract formic and acetic acids, 14.52 cc. of 0.1 *N* acetic, 9.365 cc. of 0.1 *N* formic, 10.8 cc. of 25 per cent H_3PO_4 (U. S. P. sirupy) acids, and water sufficient to make 100 cc. were extracted with ether. At the end of 19.5 hours 0.0008 gram (or 0.017 cc. of 0.1 *N*) formic acid remained to be extracted (determined by mercuric chloride reagent, *3*).

Extraction of Lactic Acid. Lactic acid (9.9 cc. of 0.1 *N*) placed in the ether extractor was diluted with water to 100 cc., and 5.5 grams of sulfuric acid (95 per cent sulfuric acid, specific gravity 1.84) were added. Two hundred cubic centimeters of ether were placed in the lower flask.

After extraction had proceeded for a certain number of hours, the electric hot plate was taken away, 100 cc. of water were added to the ether in the lower flask, and the ether was distilled off. The aqueous residue was titrated with 0.1 *N* barium hydroxide in the presence of phenolphthalein; this was allowed to stand overnight and was then filtered through No. 589 S. & S. filter paper; the precipitate was washed with water; the precipitate and filter were placed in a weighed platinum crucible and heated 15 minutes at a dull red heat. From the weight of barium sulfate in the crucible the amount of free sulfuric acid was calculated. Zinc sulfate solution (0.2 *N*) was added to the filtrate, treated on a steam bath for 6.5 hours, and filtered as the preceding solution; the precipitate and filter paper were treated as above. From the weight of zinc oxide in the crucible the amount of lactic acid was calculated.

The results of the extraction, found in Table I, show that 9.65 cc. out of 9.9 cc. of 0.1 *N* lactic acid, or 97.47 per cent, were extracted.

Table I. Results of Extraction of Lactic Acid

Time Extracted	Titer	H_2SO_4	Lactic Acid	Total Lactic Acid and H_2SO_4 according to $BaSO_4$
Hours	*Cubic centimeters of 0.1 N acid*			
6.5	6.25	0.30	6.92	7.22
9.5	2.15	0.24	2.32	2.56
9.25	0.55	0.18	0.27	0.46
8.5	0.40	0.06	0.15	0.21
7.3	0.30	0.068	0.025	0.09
41.05	9.65	0.848	9.685	10.54

Comparison of Ether Extraction with Steam Distillation

Ether extractions were made of a water solution of mixtures of the following acids: 9.696 cc. of 0.1 *N* formic, 9.365 cc. of 0.1 *N* acetic, 10.08 cc. of 0.1 *N* propionic, 9.744 cc. of 0.1 *N* lactic, 10.00 cc. of 0.1 *N* succinic, and sufficient water to make 100 cc.

In 7.5 hours 44.85 cc. of 0.1 *N* acid were extracted, consisting of about equal quantities of volatile and nonvolatile acids. During the next 20 hours the remainder of the acid (mostly nonvolatile) was extracted. Three more similar experiments showed 44.15 cc. of 0.1 *N*, 45.45 cc. of 0.1 *N*, and 49.05 cc. of 0.1 *N*, respectively, extracted in 7.5 hours.

The experiments shown in Table II demonstrate the increase in the amount of acid formed during the steam distillation of a medium. The medium consisted of one per cent Parke-Davis peptone, one per cent dextrose, one per cent dibasic potassium phosphate adjusted to pH 7.3 with sodium hydroxide. Before distillation, 25 per cent H_3PO_4 was added until the reaction was blue to Congo red.

Table II. Increase in Acid Formed

Medium	Acid per 100 cc. of Medium: Total volatile and nonvolatile	Volatile	Nonvolatile
	Cc. 0.1 N	*Cc. 0.1 N*	*Cc. 0.1 N*
Sterilized uninoculated:			
Steam	8.40	4.95	3.45
Ether	6.57	4.80	1.77
Difference	1.83	0.15	1.68
Inoculated with 90-H-1:			
Steam	48.22	8.80	39.42
Ether	32.07	....	....
Difference	16.15	....	....

These experiments show in the case of the uninoculated medium an increase of 1.83 cc. of 0.1 *N*, or 27.86 per cent by steam distillation; in the case of the inoculated medium, an increase of 16.15 cc. of 0.1 *N* or 50.36 per cent by steam distillation.

Time Required. The customary estimation of acids in bacteriological media by steam distillation involves three steps: (1) the time occupied in distillation, (2) the time consumed in the concentration of the distillate, and (3) the time involved in the ether extraction of the residue in the distilling flask.

The new method of ether extraction eliminates the time (about 10 hours) taken up by the first two steps and requires only the time for the third step; that is, both the volatile and nonvolatile acids may be extracted in the same amount of time required for the extraction by the old method of the nonvolatile acids.

Summary

Among the evidence against steam distillation may be included (A) errors caused by heat: (1) pH decrease in heating media, (2) acid increase in heating sugars with amino acids, (3) acid increase in heating sugars with mineral acids, (4) molecular changes among the organic acids—e. g., lactic to formic, and (5) failure to secure comparable data when the same medium is heated before and after the action of bacteria; (B) errors caused by incomplete separation of acids: (1) variable amounts of lactic acid may be carried over in the distillate, and (2) as much as 28 per cent of volatile acid may remain in the distilling flask; and (C) errors in concentrating distillates: acidity may be lost during the evaporation of the distillate.

The extraction of acids with ether is already successfully carried out. An apparatus is described in which formic, acetic, propionic, lactic, and succinic acids may be successfully extracted in 40 hours, and comparison of extraction by steam distillation and ether is given, showing that steam distillation may result in the formation of 27 to 50 per cent more acidity and that a large amount of time is saved by ether extraction.

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Automatic Titrating Devices

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The paper industry has a very real need for a recording titrator, for a device which will determine the total acidity of alum baths, wash waters, etc. The present potentiometric recorders do not entirely meet the need, which is for an indication of reserve acidity and not for the potential of hydrogen ions. Further, it is found that total acidity and potential are not simply or constantly related to one another under working conditions in a paper mill.

The problem has been approached in two ways: directly, by the mechanical manipulation of solution volumes; and indirectly, by the diffusive mixing of parallel liquid streams.

Direct Mechanical Titrator

A repeating cycle has been secured which comprises the following operations:

(*a*) A sample of standard volume is withdrawn from the unknown liquid.
(*b*) The sample is discharged into a reaction vessel together with a suitable quantity of indicator solution.
(*c*) The mixture is observed by an optical device which
(*d*) Controls the addition of the second component, the estimating fluid, in volume sufficient to reach neutrality, and
(*e*) Activates a pen to record the volume on a chart.
(*f*) The titrated solution is discharged to waste, the chart moved to a new position, and
(*g*) The cycle repeats.

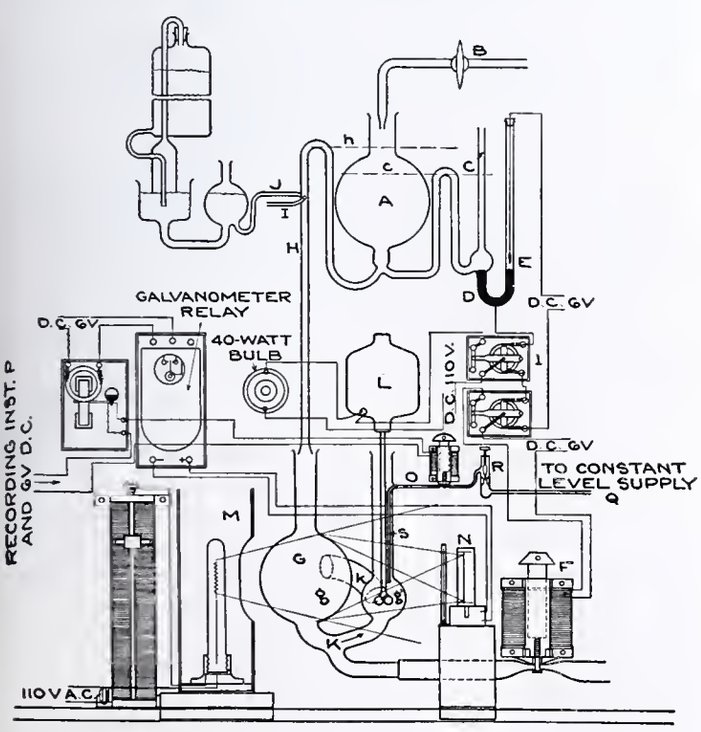

Figure 1. Diagram of Direct Mechanical Titration

The means chosen for securing the performance is illustrated in Figures 1 and 2. The first requisite, a timing unit to control the sequence of events, is provided by bulb *A* and appendages (*2*). When the bulb, which is fed with water or the unknown (dilute solution) under approximate control from tap *B*, has filled to level *c*, the solution passes over siphon *C*, loading the mercury column, *D*, which completes

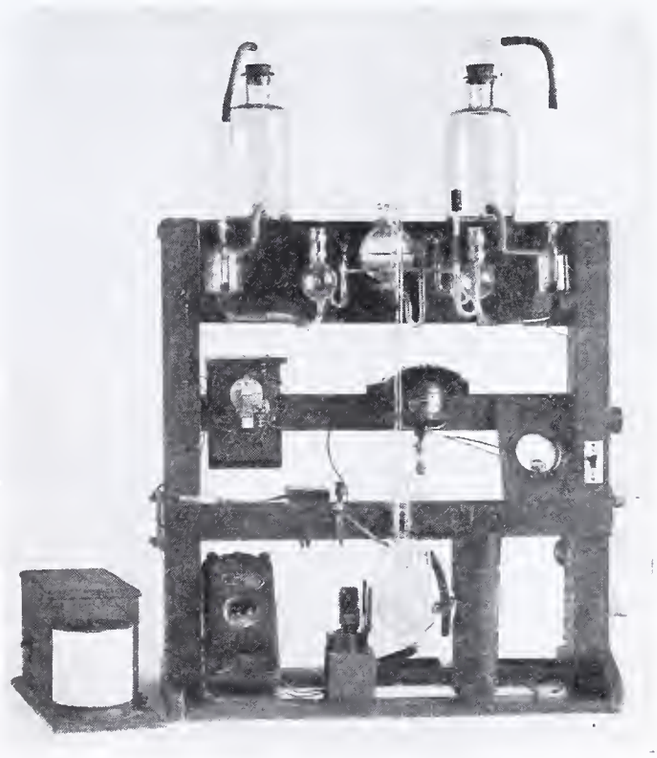

Figure 2. View of Set-Up of Titrator

a circuit through the electrode, *E*. The current actuates a magnetic valve, *F*, which allows the contents of the reaction vessel, *G*, to pass to waste. Soon after the emptying of *G*, bulb *A* should be full enough for its contents to siphon rapidly down tube *H*, unload mercury column *D*, and refill the reaction vessel. During the passage of this unit volume of fluid, a constant and repeatable suction impulse (negative pressure × time of flow) is exerted at each point in the column, notably at points *I* and *J*, from which tubes communicate with constant-level reservoirs of reagents. Through one tube a chemical color indicator (phenolphthalein, methyl red, etc.) is imbibed. The other tube is used only when pure water is fed to bulb *A*, and its purpose is to admit a predetermined quantity of the liquid to be titrated. Thus, two general levels of solution strength can be manipulated,

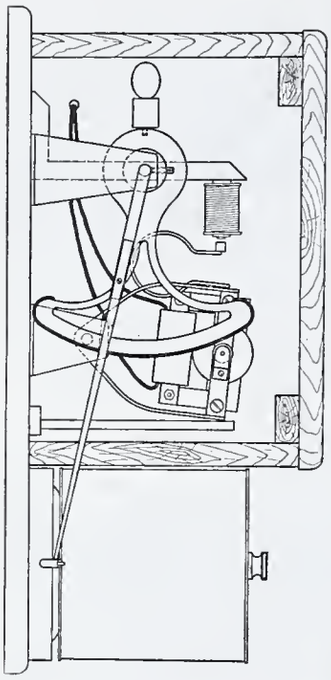

Figure 3. Diagram of Recording Mechanism

the side arm accommodating liquids containing from about 2.6 to 80 per cent of reactive material, the bulb being reserved for more dilute solutions.

The reaction vessel, G, is in two parts, a large bulb, g, and a smaller one, g', which communicate with one another by the centrally fixed lower tube, K, and the eccentrically placed return tube, k. In g', the stirring paddle, rotated by the motor, L, is stopped temporarily through relay l, which is operated in tandem with valve F each time the vessel empties. The solution is monitored by the 100-watt projection lamp, M, and the light-sensitive element, N. Since it is a change of intensity which is being observed during titration, a way must be devised to make N inoperative when the vessel is empty and is thus in its most transparent condition. In lieu of a mechanical shutter, the larger bulb is allowed to serve as a lens when full, concentrating the light from M on to N which otherwise remains relatively dark.

The cycle of operations is now continued by the electrical train in connection with N. Leaving for the moment the exact nature of the receiving element, we may assume that the action of light is to generate a current sufficiently large to operate a relay. A fraction of a second after G is full, the entrained bubbles rise to the surface, the stirrer starts and cell N provides an e. m. f. just sufficient to operate, through relays, a solenoid valve, O, and the pen of the recorder. Valve O admits the standard titrating liquid from a constant-level supply, Q, through a calibrated valve, R, and a fine tube, S, to the smaller bulb, g', where it is rapidly dispersed into the main body of the solution. The mixing lag is 1 to 1.5 seconds.

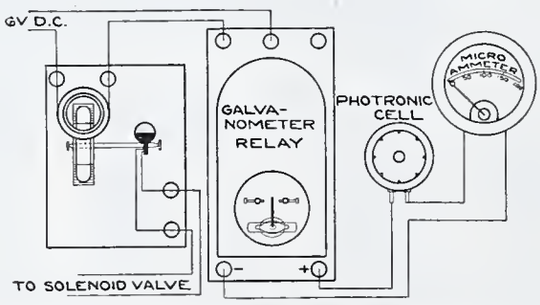

Figure 4. Arrangement of Optical Mechanism with Photronic Cell

The admission of titrating liquid under standardized conditions allows us to suppose that time and volume become mutually convertible. Hence, by recording time of addition with constant subtraction of 1.5 seconds, we record volume. The time measurement is accomplished by allowing a clock-driven pen to be actuated in series with the admission valve, so that the moment the liquid enters the reaction vessel the pen starts traveling over the chart. The admission continues till a color change is reached, when the light, becoming partially obscured by the solution, ceases to provide the minimum actuating current, the titrating liquid is shut off, and the pen returns to zero. The master flow through B is arranged so that the reaction vessel shall be emptied soon after the completion of titration, enabling the events to repeat.

Recording Mechanism. A Telechron clock motor with shaft rotating at one r. p. m. is mounted, field magnet downwards on a pivot, as shown in Figure 3. On the shaft is a small roughened wheel which can engage with the rubber facing of a quadrant, the opposite end of which carries the recording pen. The clock rests by gravity in its idle position a little to the left of the vertical, and is brought into contact with the quadrant by a lever and magnet when the latter is energized during titration. The quadrant is weighted to return the pen to zero when the magnetic pull ceases. The chart for the records is carried in a clock whose drum rotates once an hour or once a day. The records consist of a series of vertical lines (arcs) of lengths corresponding to the volume of solution addition. If the lines are drawn close together, their upper limits provide a curve of the variations in composition of the unknown liquid.

Optical Mechanism. It is plain that a gas-filled photo-cell and commercial amplifier can be adapted directly to this service and, therefore, only three alternative devices which have been used successfully in the place of such a cell will be described.

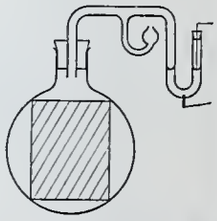

Figure 5. Crude Gas Bolometer

The new cell marketed by the Weston Electrical Instrument Corp., the photronic cell, has proved very satisfactory for titrations where detection is required of a color change visible to the eye. The diagram in Figure 4 shows the preferred arrangement. The cell is connected in series with a microammeter and a Weston contacting galvanometer, Model 30-H, 300 ohms internal resistance, 250 microamperes per mm. deflection. The controlling spring about the pivot is twisted so that the needle is held against that contact pillar which is not in use, requiring a comparatively heavy current to effect contact with the live pillar. (If this precaution is not taken the galvanometer may stick.) An adjustable resistance, carried in the lamp circuit, is set so that contact is just established when the reaction vessel is filled with clean water. The output terminals of the galvanometer are connected in series with a 6-volt battery and a Weston Mercoid relay, type 630, 6-volt, Series 118. The duty side of this relay operates the circuit for the solenoid titrator valve and the recording clock magnet.

The detail adjustment varies with the nature of the titration. When standard alkali is being run against unknown acid with phenolphthalein as indicator, a green screen (Wratten filter No. 59) is used between the vessel and the photronic cell; 95 to 100 volts across the 110-volt lamp, yielding 175 microamperes for operating the contacting galvanometer. Development of a pink color during titration reduces the current ultimately to about 80 microamperes, but the end point is considered reached at 165 microamperes, and at that point the contacting galvanometer breaks the circuit.

Many solutions which are too discolored to permit titration with the usual indicators transmit freely in the infrared. The nickel wire bolometer described elsewhere (*1*) is responsive to long-wave radiation, and can thus be used as a monitor provided a suitable indicator is available. The development of a colloidal precipitate has been found to be a simple way to absorb the infra-red, and the metals of analytical group 3 have been studied to discover an indicator for acid $\longrightarrow$ alkali titrations. Whereas aluminum and chromium salts are useless and iron salts poor, a mixture of ferric and aluminum chlorides gives a sharp end point.

From 1 to 5 cc. of the indicator solution, which consists of 30 per cent ferric chloride and 5 per cent aluminum chloride, are added to the titrated solution (250 cc.) by side tube *I* in Figure 1. At the approach of neutrality, the solution turns a deep brown and then becomes opalescent, at which point the bolometer end of balance current decreases sufficiently

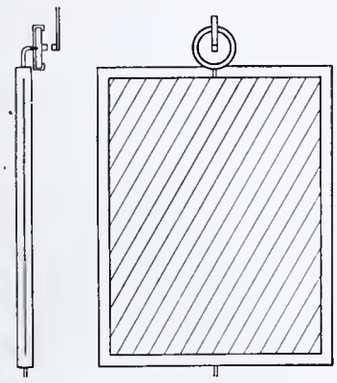

Figure 6. Improved Gas Bolometer

to actuate the relay chain, which comprises the same instruments as for the photronic cell.

The photronic cell, which operates directly and without amplification, provides sufficient energy to disturb a galvanometer needle. The movement of the needle, which represents only a fraction of the energy in the light striking the cell, suggests that perhaps the light could perform mechanical work without first being converted to electricity. The expansion of a black gas at the moment of illumination would seem a happy means to this end, but black gas mixtures are difficult of attainment and manipulation. A piece of black paper in a closed flask offered promise as a substitute. Light warmed the paper which warmed the gas in contact, and a movement was observable at the meniscus (Figure

Figure 7. Porous Tube for Indirect Visual Titration

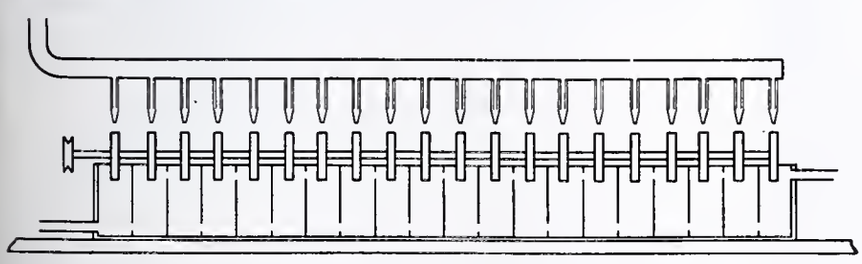

Figure 8. Chain of Cups with Indirect Visual Titration

5). When the liquid in the U-tube contained much potassium chloride, ready to complete an a. c. circuit between two copper electrodes, the device would operate the titrating unit in a crude manner.

The improvements necessary to make the bolometer independent of external temperature and pressure changes will be published elsewhere, but a modification suitable for repetitive operation warrants description at this time. In Figure 6 the receiving surface is conveniently a sheet of black gelatin emulsion stripped off a fogged and developed photographic plate. It is cemented between two pieces of glass allowing $^1/_{16}$-inch (0.16-cm.) clearance on either side. The air-tight flat vessel is connected in parallel with a rubber diaphragm controlling a sensitive electrical contact, and a breather consisting of a small U-tube having a constriction situated between two enlargements. One or two drops of a phlegmatic liquid (butyl phthalate 90 per cent, isoamyl alcohol 10 per cent) is placed in the breather. Between the near limb and the receiving chamber a wad of absorbent cotton is pushed to slow the movement of gas.

In operation, as soon as light of sufficient intensity impinges on the receiving surface the gas expands, moving the diaphragm into electrical contact. Any gas in excess of the minimum required passes out through the bubbler

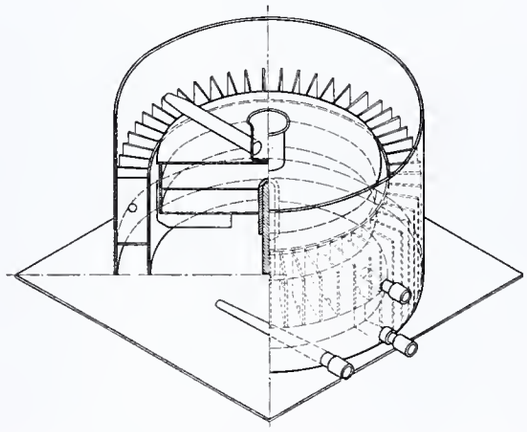

Figure 9. Circular Chain of Cups with Rotating Solution Divider

until the force is insufficient to discharge the last bubble against the surface tension of the phlegmatic liquid. There persists a slight holding pressure to maintain electrical contact. When the light is withdrawn or diminished slightly, the bubble recedes, contact is broken, and the breather then admits whatever air is necessary to establish equilibrium in the opposite direction. If the device is operated, say, every 2 minutes, the likelihood of serious change occurring in the room conditions during the interval is remote. The bolometer will operate from a 100-watt lamp, run at capacity, for a visual change such as phenolphthalein, turning from white to pink in front of a copper sulfate screen. It will operate at greatly reduced wattage with the ferric infra-red indicator.

Indirect Visual Titrator

The gradual mixing of two-solution streams to produce a color change at some point on a graduated scale offers many attractions. In a preliminary experiment a porous tube (Figure 7) was fed under pressure with acid solution, while alkali and methyl orange were passed in a uniform stream outside. It was thought that, at a distance from the entrance representing the quantity of acid necessary for neutralization, the outer solution should change from yellow to pink. Actually, the acid oozes through the earthenware to form a streamline sheath of liquid which refuses to mingle completely with the outer alkali, and the sheath is colored at its interface for its entire length. Inclusion of a fine glass rod spiral to complicate the path scarcely assists matters.

The next development involved passing one liquid through a chain of cups into which the other liquid was dropped from calibrated orifices, as shown in Figure 8. The color change

would occur sharply in one cup in a series of twenty, but only when individual stirring was provided and the jets were kept scrupulously clean. The method was impracticable in this primitive form.

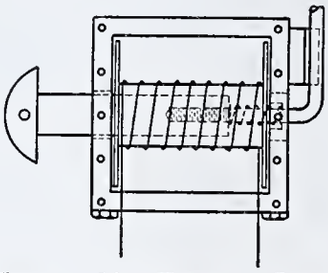

FIGURE 10. TYPICAL SOLENOID UNIT

A satisfactory instrument was constructed utilizing a circular chain of cups and a rotating solution divider for the second reagent. In Figure 9 the chain of cups is shown built into the space existing between two concentric Kodaloid cylinders (*3*). The channel is divided into fifty compartments which rise from a sloping spiral platform. The liquid is admitted into the top pocket through a calibrated jet fed from a constant-level vessel, and flows from compartment to compartment, over one barrier and under the next, until it has traversed the entire chain, whence it flows to waste. The second liquid, which should be the more dilute, is supplied, also at constant speed, to a float which rotates in a central pool of water maintained in circulation by a jet buried beneath the surface. The float is fitted with short pendant paddles which engage in the slip stream without being directly hit by the jet. From the float the liquid is discharged by a distributing pipe into the compartments, and, during any considerable period of time, is supplied to each compartment in an equal quantity. The tortuous path taken by the liquid insures mixing, and the point of neutrality is decided in one or two compartments, with a consequent error of not more than 2 or 4 per cent. A lamp is hung above the float chamber, and the compartments are numbered on the bottom in reverse writing so that the titration can be read in a mirror placed beneath the apparatus.

NOTE ON SOLENOID VALVES

The valves mentioned earlier in the paper are constructed cheaply from skeleton solenoids obtained commercially. Type CR-9503[1] a. c. 1-inch stroke, 1-pound pull is adapted for the plunger to compress, or release from compression, a piece of soft rubber tubing, which thus forms the simple acid-proof body of the valve. The solenoid is then wound with wire of a size appropriate to the voltage and purpose. A typical unit is shown in Figure 10.

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RECEIVED August 6, 1932. Communication 497 from the Kodak Research Laboratories.

[1] General Electric Catalog No. 29.

An Adjustable Stopcock Remover

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A FROZEN stopcock in a piece of apparatus is always an annoyance and frequently causes loss of considerable time and money if the apparatus is broken in trying to remove the plug from the body of the stopcock.

Allison (*1*) describes a stopcock remover which has been used by the writer to considerable advantage. A patented device (*3*) is also made and sold. Both of these have the disadvantage of having the chucks or receptacles as a series of fixed sizes, and difficulty is experienced in getting a chuck to fit properly the particular stopcock at hand.

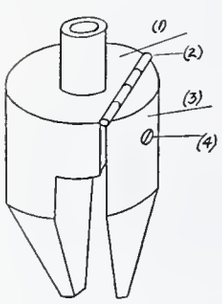

FIGURE 1

The writer has devised and used an adjustable chuck which is much more satisfactory. Complete success has been attained so far in removing plugs from a great many sizes and kinds of badly frozen stopcocks without breaking a single one.

In the adjustable chuck made by the writer, the two sections of the chuck are adjusted to fit the shoulder of the outside of the stopcock exactly, the handle of the plug remaining loose between the two sections of the chuck. In this position the chuck and stopcock are placed between the jaws of a vise or C-clamp so that a light steady pressure may be applied to the chuck and the shoulder of the stopcock on one side, and to the small end of the plug on the other side. A block of wood may be used at the end of the plug to prevent chipping. The rounded shoulder of the cock will be strong enough to withstand the pressure from the soft metal (brass) of the chuck. The light pressure thus applied will soon loosen the plug from the body of the cock. If necessary, the removal may be aided by warming the body of the stopcock with hot water or a match flame.

Where alkaline solutions have caused the sticking, the method of Ardagh (*2*) may be useful. He uses alternate suction and pressure on dilute hydrochloric acid around the stopcock. The writer has never had to resort to this procedure.

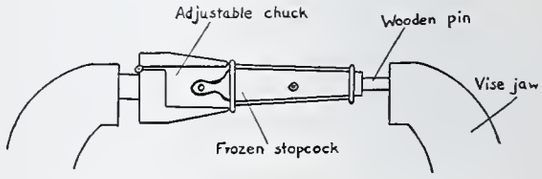

FIGURE 2

Figure 1 shows the essential parts of the chuck—1, main body which may be fastened to the stem of a C-clamp; 2, hinge; 3, movable section held in position by the screw; and 4, a compression spring between the main body and the movable section. Figure 2 shows the chuck used in a vise. This chuck may also be made to fit on the commercial stopcock remover.

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RECEIVED August 24, 1932.

Modified Hook-Up for Routine Use of Glass Electrode

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THE steadily increasing use and popularity of the glass electrode for pH determinations make it a desirable addition to any laboratory. In many instances, however, the apparatus described in the literature is not commonly available or the cost is prohibitive.

It is the purpose of this paper to describe a modified hook-up in which it is possible to use apparatus commonly available in the ordinary laboratory, achieving at the same time a good degree of accuracy in measurement and simplicity in design.

The use of the glass electrode requires the measurement of low potentials through very high resistances. The methods commonly used may be divided roughly into three groups: first, the use of a quadrant electrometer; second, the use of a condenser and ballistic galvanometer; and third, various arrangements of the vacuum-tube potentiometer. The first two methods involve the use of expensive apparatus of a type not commonly found in the average laboratory, and are subject to some experimental difficulty.

Several apparently successful types of the vacuum-tube potentiometer have been designed differing somewhat in principle. The very simple design of Elder (*1*, *2*) is based on the use of a high-sensitivity galvanometer as a current-measuring device. For some reason, probably not the fault of the method, this method seemed to be unworkable even with the special galvanometer recommended. The method of Stadie (*3*, *4*) is representative of a considerable group and is based on the Wheatstone bridge principle, using the galvanometer as a null-point instrument to indicate a balance in the bridge. Two of the resistance arms are internal (filament to plate) resistances of UX 222 tubes, and two are the external (variable) resistances of the plate circuits. If the tubes possess the same electrical properties, changes in the filament and plate batteries affect the internal resistances of both tubes alike so that the balance is not disturbed. Difficulty was met since the two tubes purchased did not have the same characteristics and the hook-up had to be further complicated to overcome this. Furthermore, two tubes which are the same at the beginning do not age equally.

Simplified Design

It was found that by substituting a variable resistance and a small potential for one of the tubes, the same accuracy was obtainable with a simpler and more compact set-up, the principle being that the potential and resistance caused a current to flow just as if it were produced in the vacuum tube. The use of only one tube obviates the preliminary calibration and comparison of tubes which is necessary if more than one is used. The design is shown in Figure 1. It will be noted that the essential parts are a potentiometer of the student type, one UX 222 tube, and a Leeds and Northrup 2420-C galvanometer, this latter being quite commonly used in hydrogen-electrode set-ups. This galvanometer has the following characteristics: sensitivity, 0.025 microampere per mm. division; coil resistance, 1000 ohms; damping resistance, 15,000 ohms.

Shielding. It was found necessary to place the apparatus on a grounded metal plate and to shield the potentiometer and the tube. The shielding was accomplished by ordinary door screening on a frame of heavy steel wire which was hinged to the back of the desk and could be raised and lowered like the lid of a trunk. The tube itself was painted with paraffin, and all sensitive parts of the apparatus were set on paraffin blocks.

Operation. The apparatus functions in the following manner:

1. The potentiometer, A, is adjusted by disconnecting the clip to the top of the tube, the standard cell connected at (1) and connection made with the ground at (2), cutting out the glass cell. The switch, Sw, is turned to connect the standard cell to the galvanometer circuit. When the potentiometer is set to read directly the voltage of the standard, there will be no deflection of the galvanometer.

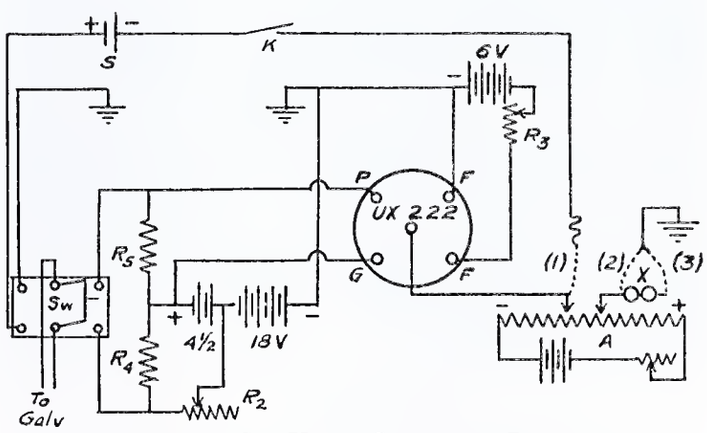

Figure 1. Set-Up of Simplified Design

S, standard cell
K, tapping key
Sw, D. P. D. T. switch
X, glass cell
R_2, 10,000-ohm variable resistance
R_3, 25-ohm rheostat
R_4- R_5, 10,000-ohm fixed resistance
A, student type potentiometer
2420-C Leeds & Northrup galvanometer

2. The tube is next adjusted to operate at its free grid potential. The standard cell is disconnected at (1) and Sw is turned to the right. The wire to the top of the tube is still disconnected. R_3 is then adjusted until the tube voltage is 3.0 volts, and after the tube is warmed up, R_2 is adjusted until there is no galvanometer deflection.

3. Connection is now made to the top of the tube and potentiometer A is again adjusted to the null point of the galvanometer, measuring the grid potential which is designated in this paper as E_0.

4. The glass electrode cell is now introduced by changing wire (2) to (3). When the potentiometer is again adjusted to the point of balance, the recorded voltage is designated as E_1. The voltage of the cell is then $E = E_1 - E_0$. In operation it was necessary to check E_0 from time to time. Results could be duplicated within ± 0.0005 volt.

Since the galvanometer is quite sensitive, it must be protected during preliminary balancing of circuits by a high resistance or shunt, as in ordinary practice. The authors found it more convenient to use a low-sensitivity galvanometer for preliminary work, switching to the sensitive galvanometer for final readings.

Measurements and Calculations

The electrodes used were of the type designed by MacInnes and Dole (*4*) using Corning 015 glass. Various arrangements

of cells have been used, but the authors found the following type very advantageous:

Satd. calomel—unknown electrode	Glass—buffer—satd. calomel known pH electrode

If E_x is the potential recorded for the cell with the unknown solution, and E_b is the potential with a buffer of known value substituted for the unknown, then

$$\Delta E = E_x - E_b = 0.0591\ \Delta\text{pH at } 25°\text{ C.}$$

To illustrate, using fresh strawberry juice and comparing it to a buffer whose pH is 3.00, when $E_b = 0.0292$ and $E_x = 0.0502$,

$$\text{pH} = \frac{0.0502 - 0.0292}{0.059} + 3.00 = 3.37$$

Comparing it to a buffer of pH = 5.00, when $E_b = 0.1483$ and $E_x = 0.0502$,

$$\text{pH} = \frac{0.0502 - 0.1483}{0.059} + 5.00 = 3.34$$

By this means measurements are rendered independent of the concentration of the buffer in the glass cell and also of the "asymmetry" potential of the electrode.

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A New Surface Tension Balance

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The measurement of surface tension is even older than the term "surface tension." Thus Guthrie (*5*) and Tate (*10*) mention that drop weights of liquids seem to bear some relation to the earlier observed phenomenon of capillary rise, but say nothing about the reasons therefor. Guthrie (*5*) postulates a picture of a film surrounding a bubble; this is advanced as a new idea, and possibly was the original thought on the subject. Since then, of course, work on surface tension by many methods and with many objects in view may be found. An excellent bibliography and comparison of methods then extant may be found in the paper by Dorsey (*2*).

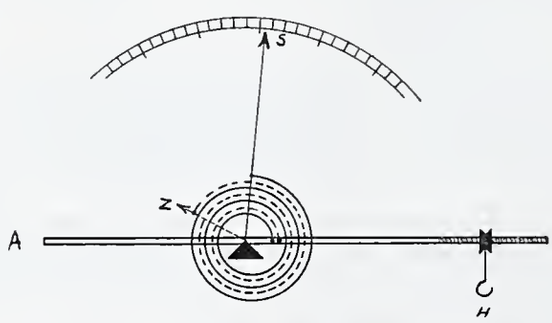

Figure 1. Diagram of Torsion Balance

Apparently detachment methods were discussed first in 1887 by Timberg (*11*), who compared the results of the measurement of surface tension by capillary rise, drop-weight, and pull-on-a-ring. The correlation was satisfactory to him, though he used the simplest of formulas to calculate the surface tension from the pull exerted:

$$\gamma = \frac{Wg}{2L} \qquad (1)$$

where γ is the surface tension, W the force necessary to tear the ring from the surface, g the acceleration of gravity, and L the length of the wire forming the ring. No corrections were applied to this formula, which really assumes that the ring raises a cylinder of liquid, though discussions of the shape of liquids raised by solid bodies may be found as far back as that of Wilhelmy (*13*) in 1863.

Further developments along this line are confined to variations in the shapes withdrawn from the liquid and corrections to be applied to the measurements. Thus we find plates, rings, spheres, rectangles, cylinders, and even evaporating dishes being used, and the formulas becoming more and more involved (*1*, *12*). Finally DuNouy (*3*) designed a surface tension balance similar in principle to Timberg's (*11*), but by his wide application of this balance, particularly in the physiological field, he popularized the method. His results were calculated by Timberg's simple formula (Equation 1), probably because of the intricacy of all correction formulas derived up to that time by the many investigators.

In this country detachment methods have been confined to the ring method, possibly because of the popularity of the DuNouy balance, but in Germany the bent-wire method has found favor. In both methods the general scheme for the attainment of absolute results was to measure a liquid whose surface tension was known from some other, more accurate method, and adjust all other readings accordingly. The bent-wire method was raised to the eminence of an absolute method by the theoretical derivation of corrections by Lenard (*9*) and measurements by Dallwitz-Wegener and Zachmann (*9*) checking the theory against practice. A similar step in the development of the ring method did not come, however, until 1930, when accurate measurements of correction factors to be applied to this method by Harkins and Jordan (*6*) were combined with a derivation of the corrections for the curvature of the column of liquid raised by the ring by Freud and Freud (*4*). Since the theory yields the same factors as did comparison with values obtained by the capillary-rise or drop-weight methods, the ring method may now stand on its own values as an absolute method of surface tension, of inherent accuracy practically equal to that of other methods, and rapidity and convenience exceeding most others.

Theory of the Torsion Balance

The work of Lenard et al. (*9*) was performed with a torsion balance. The work of Harkins and Jordan employed a modified chainomatic balance. Since the torsion balance had been so successful in the bent-wire method, it was hoped that it could be applied as well to the ring method, employing as many of Harkins and Jordan's precautions as would be commensurate with practical applications, yet retaining the inherent advantages of great speed with high accuracy of this type of instrument. A direct-reading instru-

ment was desired, if possible, so that the value of dynes per centimeter might be obtained without calculation. This means that compensating devices for correcting slight differences in the lengths of rings and in the change of acceleration of gravity must be devised. To do this, the basic theory of a torsion balance must be considered.

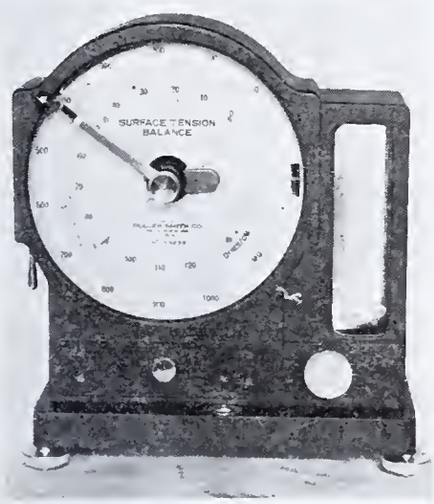

FIGURE 2. BALANCE AS BUILT

Two springs carry the load on the balance. One spring is fastened to the beam and to the index finger, so that as this moves over the scale more and more force is exerted upward on the right-hand side of the beam, thus balancing the force of gravity acting on the load which is suspended from the hook H. The second spring is attached to the beam and to an auxiliary handle by means of which constant loads or tares may be compensated for by the exertion of a constant force to balance them. Any change in g or L (Equation 1) affects γ geometrically, so the zero adjuster cannot compensate for such conditions. The simplest method of adjustment is variation of the length of the balance arm A, accomplished by threading the hook on the arm, thus permitting the load to be moved out or in as the readings are to be higher or lower, respectively. The balance as designed and built is shown in Figure 2.

It now remains to devise some method whereby the hook may be moved to its proper position so as to yield direct readings. The difficulty is that movement of the hook changes the torque due to the weight of the hook itself and the zero adjuster must be varied accordingly. No simple ratios apply, therefore, and more complicated equations must be sought. A skeletonized balance arm is shown in Figure 3. A load W and the weight T of the hook and any unbalancing t of the balance arm itself may be considered as making up the total downward pull on the arm. Whether the balance arm is unbalanced, and which side is heavier is immaterial: if the load t is considered as being concentrated at distance a from the fulcrum, moving the hook does not change this load. Movement of the hook does change the length of arm A and varies the torques exerted by weight W and tare T. This downward torque is balanced by the two springs. The torque exerted by the zero adjusting spring may be called Z and that of the second spring X. When the balance was built, a spring of certain modulus was combined with a scale of certain size. Whatever the values, the torque X exerted by the spring is translated into scale reading S by a factor f, or $X = fS$.

Equating upward and downward torques,

$$fS + Z = at + (W + T)A \qquad (2)$$

If the balance is set properly, with zero load ($W = O$) the balance will be in equilibrium when the scale reading is $O(S=O)$. Hence

$$O + Z = at + O + AT \qquad (3)$$

or

$$fS = AW \qquad (4)$$

and for direct reading,

$$S = W, \text{ so } f = A \qquad (5)$$

A necessary condition for direct reading is that A must equal f.

By algebraic manipulation of Equations 2 and 5 other expressions may be obtained on which the method of setting the balance for direct reading is based. The derivations of these equations are simple and will not be given. The methods and final equations follow:

To find T: with no load, adjust the zero; add weight W and obtain reading S_1; move suspension hook in or out and obtain reading S_2; remove W and adjust the zero. Replace W and obtain reading S_3. The value of T may be found from

$$T = \frac{S_3 - S_2}{S_1 - S_3} W \qquad (6)$$

T is a constant inherent in a given balance, and once determined may be used whenever desired. Knowing T, the balance may be set as follows: with no load, adjust the zero; add weight W and obtain reading S_1; calculate S_2 from

$$S_2 = (W + T)(1 - S_1/W) \qquad (7)$$

Move the hook until reading S_2 is obtained, remove the weight W, and adjust the zero. The balance is now ready to read directly in milligrams.

APPLICATION TO SURFACE TENSION

Harkins and Jordan (*6*) modify Equation 1 by including a factor F which depends on several variables. Thus Equation 1 becomes

$$\gamma = \frac{Wg}{2L} F \qquad (8)$$

If the balance is to be equipped with a scale reading in dynes per centimeter, Equation 8 should give the relation between

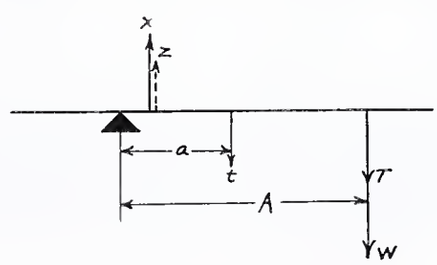

FIGURE 3. SKELETONIZED BALANCE ARM

such a scale and the milligram scale. F bears no simple relation to W, and must be applied separately; no scale could be made easily to include F. Using $g = 981$ and $L = 4.000$ cm.,

$$\gamma = 981W/8$$
$$1 \text{ dyne/cm.} = 8.1555 \text{ mg.} \qquad (9)$$

Thus if the balance is set to read directly in milligrams, the relation between the surface tension and milligram scale should be as shown above. In order to mark the scales accurately, a dividing engine was used whose head did not carry parts of the circle permitting such a ratio, so the factor actually employed was

$$1 \text{ dyne/cm.} = 8.146 \text{ mg.} \qquad (10)$$

The result of this variation and of many other errors will be discussed after the remaining calculations have been outlined.

The remaining calculations are merely adapting the data of Harkins and Jordan (*6*) to the special conditions obtaining here. In their Table VIII, F is given as a function of R^3/V and of R/r, where R is the (average) radius of the ring, r the (average) radius of the wire forming the ring, and V the volume of liquid raised by the ring. The length of the wire is taken as 4.000 cm. and the diameter of the wire as 0.0140 inch, or 0.01778 cm. Hence

$$\begin{aligned} R &= 4/2\pi = 0.63661 \text{ cm.} \\ r &= 0.01778 \text{ cm.} \\ R/r &= 35.805 \end{aligned} \tag{11}$$

In Harkins' Table VIII the values of F are given for values of R/r of 34 and 36: values of F corresponding to an R/r of 35.8 are obtained by interpolation.

When the rupture of the film occurs, the weight of the liquid suspended from the ring and raised above the surface of the main body of liquid just exceeds the tension of the surfaces at the ring. If this break occurs at a scale reading of S dynes/cm. and the balance is set properly to read directly in milligrams, then by Equation 10 the weight of the liquid raised is

$$W = 0.008146\, S \text{ grams}$$

and if D is the density of the liquid, the volume raised is

$$V = 0.008146\, S/D \text{ cc.}$$

Hence

$$R^3/V = 31.672\, D/S \tag{12}$$

To tabulate values of F for given values of S is impossible, since F depends on R^3/V, and this in turn involves D, which is specific for each liquid and temperature. However, we could tabulate values of S/D against the corresponding values of F by calculating R^3/V from Equation 12. This, with the value of R/r given in Equation 11, will permit the interpolation of the corresponding value of F from Table VIII in the article by Harkins and Jordan (*6*). These values are given in Table I.

Table I. Correction Factors *vs.* S/D

S/D	0	1	2	3	4	5	6	7	8	9
100	1.020	1.021	1.023	1.025	1.026	1.028	1.029	1.030	1.032	1.033
90	1.005	1.006	1.008	1.009	1.011	1.012	1.014	1.015	1.017	1.018
80	0.987	0.989	0.991	0.993	0.995	0.996	0.998	0.999	1.001	1.003
70	0.969	0.971	0.973	0.975	0.977	0.979	0.981	0.982	0.984	0.986
60	0.952	0.953	0.955	0.957	0.959	0.960	0.962	0.964	0.966	0.968
50	0.933	0.935	0.937	0.939	0.941	0.942	0.944	0.946	0.948	0.950
40	0.912	0.915	0.917	0.919	0.921	0.923	0.925	0.927	0.929	0.931
30	0.887	0.889	0.891	0.894	0.897	0.899	0.901	0.904	0.907	0.910
20	0.856	0.860	0.864	0.867	0.870	0.873	0.876	0.879	0.881	0.884
10	0.797	0.806	0.814	0.822	0.828	0.834	0.839	0.844	0.848	0.852
0	...	...	...	...	...	...	...	...	...	0.787

Since the dynes/cm. scale was formulated on the basis of Equation 8 without the F (which then is Equation 1) the scale reading S is

$$S = \frac{Wg}{2L}$$

and from Equation 8

$$\gamma = \frac{Wg}{2L} F$$

Hence

$$\gamma = SF \tag{13}$$

Therefore, by dividing the reading S by density of liquid D, the value of F may be read in Table I. Then F times S gives the true surface tension γ as based on the empirical corrections of Harkins and Jordan (*6*), which in turn were justified by Freud and Freud (*4*) on purely theoretical grounds.

Sources of Error

Harkins and Jordan (*6*) claim an accuracy for the ring method, using their corrections, of 0.25 per cent. The accuracy of the interpolated values of the correction factors themselves is not claimed to be better than 0.4 per cent. Hence the error in the final value of γ (Equation 13) will be the square root of the sum of this error in F, squared, plus the error in S, squared. It remains to evaluate the error in S.

1. Error due to the wrong relation between the two scales, as shown by Equations 9 and 10: Equation 8 shows that S is directly proportional to g. Equation 10 really assumes a value of g of 982.2, so if we take 981 as the correct value, the error in g will produce an equal error in S, or

$$\text{Error} = (982.2 - 981.0)/(981) = 0.12\%$$

2. Error in R: R, or rather L, to which R is directly proportional, is guaranteed to ± 0.1 per cent. Any error in R changes R/r, R^3/V, and L.

a. Effect of error in R on R/r: A variation of 0.1 per cent in R produces an equal variation in R/r. The effect of this change on the value of F interpolated from Harkins' Table VIII is at the maximum 0.0002, or 0.03 per cent. This is negligible, and in the following calculations a value of R/r of 35.8 will be used as before, and Table I remains applicable.

b. Effect of error in R on R^3/V and on L: No simple relation applies here, so let us assume actual figures and calculate the errors produced by variations in these figures.

Assume water at 20° C. gave a reading $S = 74.6$. The density is 0.9982. Using a value of R of 4.004 cm., we can calculate the actual value of γ which was measured:

(Equation 10) $W = 8.146 \times 74.6 = 607.7$ mg.
$V = 0.6077/0.9982 = 0.6088$
$R^3/V = 0.2588/0.6088 = 0.425$
(Harkins' Table VIII) $F = 0.977$
(Equation 8) $\gamma = \dfrac{(0.6077)(981)}{8.008}(0.977) = 72.74$

However, we would normally calculate the value of γ from Table I:

$S = 74.6$ $D = 0.9982$
$S/D = 74.73$
(Table I) $F = 0.978$
(Equation 13) $\gamma = SF = 72.96$
Error $= 0.30\%$

3. Error in r: The size of the wire is specified as 0.0140 ± 0.0001 inch. Assuming r to be 0.0141 inch, or 0.017907 cm., we find R/r to be 35.551 instead of 35.8. From Harkins' Table VIII we find that this change produces a maximum variation in F of 0.25 per cent.

4. Error in density: For benzene at 20° C. a change of 6 in the third place in the value of the density is required to vary the value of F 1 in the third place. Hence an error in density of 0.07 per cent affects γ to 0.01 per cent.

5. Error in temperature: The effect of change in density with temperature is so slight that the final effect on γ is negligible, as stated above. For water the value of γ varies 0.14 per cent per degree Centigrade at 20° C. Without apparatus such as described by Harkins and Jordan (*6*) the ring method is notoriously weak in the matter of temperature control. For work of ordinary accuracy, however, variations of less than 1° C. are negligible. The simple expedient of opening and closing windows has sufficed to maintain the room in which this instrument is used to within 1° C. with very little trouble.

6. Compensation of other errors: This balance was designed with adjustable features in order that it might be set to give correct readings.

Under the discussion of error 2*b* a sample set of data was used and γ showed to be in error by 0.30 per cent, if the error in R be ignored. In setting the balance, however, the reading 74.6 would be considered unsatisfactory and the hook would be moved out until the break occurred at 74.4 instead, for at this value

$$S = 74.4 \qquad D = 0.9982$$
$$S/D = 74.53$$
$$F = 0.978$$
$$\gamma = SF = 72.76$$

That is, the balance now gives correct values for water and any other liquid in that range of surface tension. This was accomplished by lowering the readings 74.4/74.6, or 0.9973 times the old values: this invalidates Equation 10.

Measuring a liquid of true surface tension of 29.00 dynes/cm. and density 0.879, if the balance were still set for direct reading in milligrams, Equation 10 applies and the reading at which the break occurred may be calculated to be 32.2. Had the balance not been properly set for water, the value of γ found would be

$$S/D = 32.2/0.879 = 36.6$$
$$F = 0.903$$
$$\gamma = SF = 29.08$$
$$\text{Error} = 0.24\%$$

However, in the adjustment the readings were changed by the factor 0.9973, so the break would now occur at a reading of

$$S = 32.2 \times 0.9973 = 32.1$$
$$S/D = 36.5$$
$$F = 0.903$$
$$\gamma = SF = 28.99$$
$$\text{Error} = 0.07\%$$

That is, setting the balance to read correctly for water corrects the readings in the neighborhood of the majority of organic liquids to less than 0.1 per cent error.

By similar calculations it may be shown that moving the hook to eliminate the error due to variation in r (which was 0.25 per cent) in the neighborhood of 70 dynes/cm. also corrects readings in the neighborhood of 20 dynes/cm. to within 0.01 per cent.

7. Miscellaneous errors: Harkins and Jordan (*6*) mention other sources of error such as tilting the ring out of the plane of the surface, lack of cleanliness, insufficient area of surface, etc. Such errors involve technic rather than theory and must be left to the intelligence of the operator.

Klopsteg (*8*) points out that a considerable error may be introduced if the balance is not in its equilibrium position at the moment of rupture. He also discusses the importance of correcting for the weight of droplets of the liquid adhering to the ring after the rupture. The more recent work of Harkins and Jordan (*6*), however, considers this correction to be erroneous.

Concerning the area of surface, DuNouy (*3*) states that the minimum diameter of the watch glass used for a containing vessel is 5 cm. when a ring of 4-cm. circumference is used. The balance as designed accommodates a 6-cm. watch glass, or, if the door is open, an 8-cm. glass may be used. If the liquid tested wets glass, DuNouy states that 3.5 cm. diameter of containing vessel is sufficient. The use of a 5-cm. glass resting on an 8-cm. glass allows overflowing of the surface of the liquid and tends to insure cleanliness of surface.

To summarize the errors; by adjusting the hook the variations in R and r may be compensated for to 0.1 per cent. In the example used it will be noted that the error in the scale relation was included tacitly; this, too, is compensated for and included in the 0.1 per cent. The error due to density was 0.01 per cent, and that due to temperature 0.14 per cent. It is obvious that temperature control is the greatest need. Applying the Theory of Errors, the combined effect of these errors on the value of S may be calculated by the square root of the sum of the squares and found to be 0.2 per cent. Since

$$\gamma = SF$$

and the error in F was given as 0.4 per cent, the error in γ may be calculated similarly to be less than 0.5 per cent.

Setting the Balance

If the values of R, r, and g are correct, the balance may be set to read directly in milligrams, and the surface tension readings will also be found to be correct. If any of these factors is in error, the hook must be moved to compensate for that error.

Water is the usual standard for surface tension work. If it is known what reading should be obtained so that, when properly corrected (by Table I), it equals the true surface tension of water at the desired temperature, then the hook may be moved out or in until the rupture occurs at the reading desired, and the balance will be set for direct reading in dynes per centimeter for any liquid. For this adjustment of the hook, T should be found in dynes per centimeter from Equation 6 and then S_2 calculated from Equation 7, using as W the desired reading in dynes per centimeter.

Table II gives the apparent values of the surface tension of water at various temperatures. If the rupture occurs at the value given in Table II, the reading when corrected will be the true surface tension of water (*7*).

Table II. Apparent Values for the Surface Tension of Water

° C.	Dynes/cm.	° C.	Dynes/cm.
18	74.6	22	74.1
19	74.5	23	74.0
20	74.4	24	73.9
21	74.3	25	73.7

For work confined to a narrow range of values of surface tension, a simpler adjustment may be made. Thus, if the hook is moved until the rupture occurs at a reading equal directly to the true surface tension, F is automatically included in the reading and the balance may be used to read directly with no correction whatsoever. Thus, if set for water at 21° C., the value of F included in the setting is 0.977, and the balance may be used from γ equals 71 to 77 dynes/cm. with a maximum error of 0.5 per cent. A balance set to read directly on water, however, would be in error by 14.3 per cent when measuring the surface tension of benzene.

Experimental Results

In order to check the equations derived, the balance was set to read directly in milligrams and then used to determine the surface tensions of water, benzene, glycerol, and carbon tetrachloride. The setting of the balance to read in milligrams showed Equations 6 and 7 to be correct. The results are given in Table III.

Table III. Experimental Results of Balance Readings

(Temperature, 20° C.)

Liquid	Actual Reading	Density	Corrected Reading	I. C. T.
H_2O	74.4	0.9982	72.7_7	72.75 ± 0.05
C_6H_6	32.0	0.8788	28.8_7	28.88 ± 0.03
$C_3H_8O_3$	67.2	1.221	63.3_6	63_4 ± 3.0
CCl_4	31.3	1.594	26.7_4	26.77 ± 0.1

Acknowledgment

Much credit must be given the Roller-Smith Company, Bethlehem, Pa., which so successfully translated the theoretical requirements into actual fabrication of the desired instrument.

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Micromelting-Point Determination with the Thiele Tube

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A HOT stage, though a requisite in microwork, is not always available for melting-point determinations. In its place an ordinary Thiele tube or one of the various modifications of the tube (*1*, *2*, *3*) may be substituted. If an electrically heated tube, as devised by Sando (*6*), is available, it can be utilized. Otherwise the tube is heated in the usual manner by means of a small flame.

The apparatus is shown in detail in Figure 1. Two glass rods are fused to the side walls of the tube containing the sample and thermometer to support it in the Thiele tube. To observe the melting point optically, a microscope—preferably a reading microscope, as used in optical experimentation—is turned to a horizontal position and the stage removed to make room for the Thiele tube. The sample is placed between two small squares cut from a microscope cover glass with a diamond point, or, in the absence of a diamond point, broken by hand. One 18 by 18 mm. cover glass will yield six small squares sufficient for three melting-point determinations. The glass slips, with the sample between, are held in position by a small clip made of thin platinum wire.

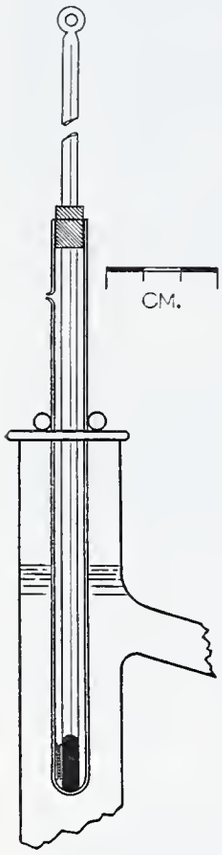

Figure 1. Detail of Apparatus

Procedure

The sample, contained between the sections of cover glass, is placed in the empty tube and supported vertically by means of the thermometer which is subsequently inserted. The thermometer is secured in the tube by means of a small roll of asbestos paper. The tube is now inserted in the Thiele tube.

The sample should be well illuminated. Temperature readings and the progress of melting of the material under test can be simultaneously observed by means of an Abbé drawing camera. A 32-mm. objective possesses a sufficiently long working distance to focus on the sample and at the same time avoid undue heating of the objective due to the proximity of the hot Thiele tube.

The customary precautions essential to a determination should be observed (*4*). The temperature of the bath liquid, in particular, should be very gradually increased. The usual bath liquids may be used (*5*). Snell (*7*) has proposed the use of phosphoric acid. Water is preferable to sulfuric acid for substances melting at less than 100° C. To correct the observed melting point, recourse is had to a calibration curve based on the observed and corrected melting points of several materials.

Calibration

To calibrate the instrument several materials of corrected melting point are taken and their melting point in the apparatus observed. A calibration curve is drawn for subsequent work. Table I presents the results of several determinations, from which a graph may be constructed.

The differences between the observed and corrected melting points are small at low temperatures because of the small stem exposure in the case of the corrected melting point. At higher temperatures the protecting action of the tube surrounding the thermometer becomes apparent, the corrections being smaller than when the thermometer is directly immersed in the Thiele tube. Since the calibration curve is specific for each individual instrument and empirically dependent upon the dimensions, depth of immersion, etc., the apparatus has been designed to take care of these effects automatically. The projecting lugs of the tube permit it to be inserted to the same depth at each observation; the thermometer should always be inserted till it touches the bottom of the tube. The size of the aperture in the wall of the tube produces a discernible effect on the melting point: a very small hole gives a low melting point, and a very large hole gives a higher melting point on the same material. The only variable factor is the height of the bath liquid. This should be regulated by keeping the bath liquid level with an etched ring on the Thiele tube. Sulfuric acid will require no attention for long periods of time; water, particularly at high temperatures, will require leveling more frequently. The instrument requires no external support for the thermometer, the lip of the Thiele tube being ground flat to insure the stability of the tube and thermometer.

Table I. Calibration Data and Typical Determinations of Melting Point

Material	Observed Melting Point Micro-Thiele Tube	Correction from Graph	Corrected Melting Point	Corrected Melting Point Standard Method	Melting Point in Literature
	° C.	° C.	° C.	° C.	° C.
Thymol	51.0	0.3	51.3	51.3	51.5
Naphthalene	80.2	0.6	80.8	80.8	80.8
Benzoic acid	121.0	1.3	122.3	122.3	122.5
Urea	130.9	1.5	132.4	132.4	132.5
Anthracene	211.6	4.0	215.6	215.6	216.0
Phenolphthalein	253.6	6.4	260.0	260.0	261.1
Silver nitrate	205.1	3.8	208.9		209.0
Salicylic acid	157.5	2.0	159.5		159.8

Advantages of Instrument

The preparation of capillary tubes, usually regarded in the light of a task, is entirely eliminated. The operation of placing a minute quantity of sample between two glasses is infinitely easier than filling a melting-point capillary. A small amount of material spreads over a larger area and its melting point is much sharper between two glasses than when examined in a capillary. This instrument is superior to a hot stage for rapid work, since the inner tube and thermometer can be quickly transferred to a cold Thiele tube for subsequent determinations, whereas a hot stage is so thoroughly insulated as to retain its heat for a long period of time.

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A Color Test for Rotenone

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THE increasing use of rotenone as an insecticide renders methods of testing for this material of great importance. In a review of the literature it was found that Durham (*1*) in 1902 had discovered a peculiar color reaction of rotenone which showed promise of being a good qualitative test for the material. When he treated rotenone, either the crystals or powder, with a drop of concentrated nitric acid on a glazed porcelain plate, it became red. The addition of a few drops of strong ammonium hydroxide gave a deep, greenish blue color, which quickly faded to yellow.

In this form the reaction is unsuitable for delicate testing because of the violence of the neutralization and the extremely rapid disappearance of the blue color. In the course of the present study it was found that when an acetone solution of rotenone is treated with 1 to 1 nitric acid it gives a bright red color which on addition of ammonium hydroxide changes to the characteristic blue color. This procedure makes the test more delicate and more suitable for general use. Other alkaline reagents, such as solutions of sodium and potassium hydroxides and sodium and potassium carbonates, give the same color. Such weakly alkaline materials as sodium bicarbonate and borax do not produce it.

All attempts to render the blue color permanent have thus far failed. However, it was found that dilution with water after the nitric acid reaction rendered the blue color developed with ammonium hydroxide somewhat more lasting. Neutralization of the acid with sodium bicarbonate followed by the addition of the ammonia gave an even more lasting blue color. Even this, however, faded in the course of 2 or 3 minutes.

The method finally adopted as most suitable for a qualitative test consists of the following steps:

One cubic centimeter of an acetone solution of rotenone is treated with 1 cc. of 1 to 1 nitric acid, and the mixture allowed to stand for 0.5 minute. It is then diluted with 8 to 9 cc. of water and 1 cc. of strong ammonium hydroxide added. A blue color is produced which is almost identical with that given by bromothymol blue indicator at a pH of 7.2. As little as 0.1 mg. of rotenone can be detected by this method.

Several pure materials related to rotenone were tested by the method just outlined, to see if they would interfere. One milligram of material per cubic centimeter of acetone solution was used. Deguelin gave a test apparently identical with that given by rotenone. Tephrosin gave no blue color, and toxicarol only a very faint blue as compared with a deep blue for rotenone at this concentration. Dihydrorotenone, isorotenone, and rotenone hydrochloride also gave about the same depth of blue color as rotenone. Dehydrorotenone and rotenonone, oxidation products of rotenone, gave no blue color. Acetone extracts of pyrethrum flowers and tobacco did not give the test.

Tephrosin gave a faint blue color when concentrated nitric acid was allowed to act on the dry material, the remainder of the procedure being as above. Tested in this way toxicarol gave a deep purple color.

Naturally it was hoped that this color test might prove adaptable to a quantitative colorimetric method for the determination of rotenone. The principal difficulties were the marked dependence of the depth of color on the temperature and time of reaction, and the rapid fading of the blue color. By controlling the reaction conditions it was not difficult to reproduce about the same intensity of blue color. At first standard rotenone solutions were run simultaneously with an unknown, but this proved entirely unsatisfactory because of inability to manipulate the addition of reagents to the several tubes at the same time. A standard series of color solutions containing different concentrations of bromothymol blue in a buffer of pH 7.2 was then prepared. These solutions were standardized against the colors produced by different amounts of rotenone. By using the test as previously outlined, or better, by neutralizing the acid with sodium bicarbonate solution, the color obtained was sufficiently stable to allow of a hasty comparison with these standard colors. In this way the test may be used to give a rough estimate of the amount of rotenone present. However, it will have no value as an exact colorimetric method unless some means is found of rendering the blue color much more lasting.

The exact nature of the chemical reactions upon which the test depends is not known at present. The nitric acid produces at least two compounds, of which one, red in color, is extractable from sodium bicarbonate solution by means of ethyl acetate. It is this one which, while stable in acid or nearly neutral solution, becomes blue and unstable in alkaline media. It contains nitrogen in some form.

This color test has been used in the Insecticide Division for surveying plants as sources of rotenone, acetone extracts of the plants being made and tested as outlined above. As stated before, deguelin, a natural constituent of some plants which are sources of rotenone, also gives the test, but deguelin is also of value insecticidally, so that any plant material which gives a definite color test is worthy of study for its insecticidal properties. A direct test on plant material may also be made by placing several drops of concentrated nitric acid on the sample, allowing it to react for 0.5 to 1 minute, and then adding several drops of ammonium hydroxide. Roots containing as little as 1 per cent rotenone gave an evanescent blue color in this way. It is suggested that this form of the test might be used by field expeditions and plant explorers.

The test has also proved useful in determining the completeness of extraction during recovery of rotenone from derris and cubé roots; in detecting rotenone in spray resi-

dues; and in following the course of decomposition of thin deposits of rotenone exposed to light and air, an adaptation rendered possible by the fact that the test is not given by the products of such decomposition.

The testing of proprietary insecticidal preparations is an obvious use for this method. In the case of dry powdered preparations the test may be made on an acetone extract. Liquid preparations and extracts including oily samples usually respond to direct treatment with nitric acid.

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Use of Kohlrausch Sugar Flasks in Determinations of Biochemical Oxygen Demand

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Kohlrausch sugar flasks were first advocated for putrescibility tests in 1928 by Pomeroy and Stone (*3*), thus applying the principle of the constricted tube with marble seal devised by Hall (*1*, *2*) in 1915.

These flasks are equally suitable for biochemical oxygen demand tests and are much more convenient than the reagent bottles. It is difficult to replace stoppers in reagent bottles without trapping air bubbles, and more care is required with the reagent bottles in disposing safely of the excess of liquid forced out upon the addition of reagents, although these objections do not apply to the special flasks devised by Theriault (*4*, *5*).

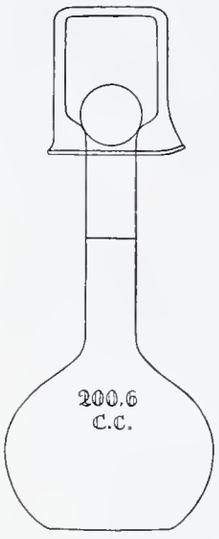

Figure 1. Kohlrausch Sugar Flask with Marble Seal and Beaker

With the Kohlrausch flasks air bubbles are also easily excluded; the excess of liquid is caught above the marble seal and can be easily dumped in the sink when the flask is inverted, with the finger holding the marble in place to mix its contents. The author has worked with flasks of 200.6 cc. calibrated capacity, holding about 225 cc. to the marble seal. The graduation is an advantage in measuring samples for titration. During incubation evaporation is minimized by means of an inverted beaker, as shown in Figure 1. The flask has one disadvantage, that its shape slightly delays thorough mixing as compared with bottles, and necessitates special attention in securing thorough diffusion of reagents. If Kohlrausch flasks should receive favor for these tests, an improved form with a short neck would overcome this one objection. In the writer's experience the results of comparative determinations of biochemical oxygen demand on single samples showed less variation with flasks than with bottles, but further comparative studies are needed and particularly by those accustomed to using bottles.

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A Continuous Extractor

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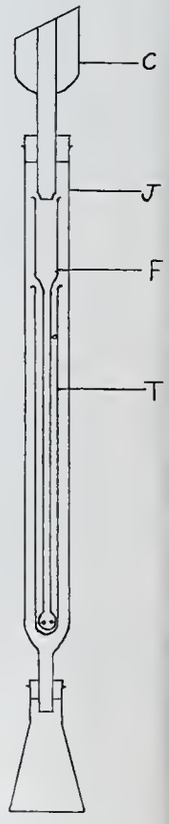
The usefulness of a continuous extractor, especially in the analysis of biological fluids such as urine and blood filtrates, is being gradually recognized. A form of extractor which the author has found highly satisfactory is given in the accompanying sketch. It consists of an outer jacket, *J* (length, 450 mm.; internal diameter, 32 mm.); an extraction tube, *T* (length, 280 mm.; internal diameter, 15 mm.), having a 5-mm. opening 45 mm. from the top of the tube; a funnel tube, *F* (length 340 mm.; external diameter 7 mm.), with a bulb at the lower end containing four small openings; a condenser, *C;* and a 125-cc. Erlenmeyer flask. The extraction tube is suspended by means of a silk thread or a thin wire.



This tube is designed for a sample of 20 cc. or less. A battery of six to eight extractors can easily be set up. At the completion of the extraction, the flask is removed, fitted with an ordinary distilling head, and the solvent removed by distillation.

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Increased Shipments of U. S. Biological Preparations to Philippines. Modification by the Philippine Health Service of its regulations affecting the period of potency of biological preparations is expected to react to the advantage of American exporters of such products, according to the Commerce Department.

Changes in the Philippine regulations bring them into line with the regulations of the United States Hygienic Laboratory. Formerly, European manufacturers could comply with the Philippine regulations because it usually meant only shortening their datings, while American manufacturers, prohibited from lengthening their datings, found it difficult to compete.

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Analysis of Refrigeration-Grade Liquid Sulfur Dioxide

Official Method of the Sulfur Dioxide Committee, Compressed Gas Manufacturers' Association

Introduction

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Chairman, Sulfur Dioxide Committee, Compressed Gas Manufacturers' Association

THE experience of the refrigeration industry has demonstrated that extreme refinement in the purity of liquid sulfur dioxide that is to be used as a refrigerant in automatic refrigerating machines is commercially very important. Obviously, therefore, it has become important to determine reliably the exact degree of purity of this product, in which all impurities occur only in very minute quantities. Accuracy of analysis of from one to two parts per million is required.

The manufacturers of refrigeration-grade liquid sulfur dioxide, wishing to avoid controversies in this matter of the purity of their products, created a special committee of chemists to draft a standard procedure for the analysis of liquid sulfur dioxide. The chairman of this committee was F. B. Downing of E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., the other members being L. S. Larsen of Ansul Chemical Co., Marinette, Wis., and A. K. Scribner of the Virginia Smelting Co., West Norfolk, Va. The committee considered all the data that had been collected by the manufacturers represented, and after a year's work completed its draft of a standard method of analysis. This was submitted to the full Sulfur Dioxide Committee of the Compressed Gas Manufacturers' Association, which was aided by a representative of the Calco Chemical Co., who was not a member of the association. The report was approved with very minor changes, and then referred to the Governing Board of the Compressed Gas Manufacturers' Association, which approved it as the tentative standard of the association.

The manufacturers regard it as the standard method to be used for all control analyses. The method is given in detail below.

MOISTURE

Sulfur dioxide for the refrigeration industry is usually guaranteed to contain less than 50 parts per million of moisture, while the actual moisture content may be as low as 5 parts per million in some cases. This represents from 0.0025 to 0.025 gram per pound of product (453.59 grams). The accurate determination of this small amount of moisture (*1*, *2*) presents difficulties, in that the detailed technic and the exclusion of outside moisture must be carefully controlled to obtain correct results. The method in outline is simple; a sample of liquid sulfur dioxide is drawn from the cylinder or drum in question and allowed to evaporate through a tared phosphorus pentoxide tube whose gain in weight is taken as the moisture content of the sample.

Under the best conditions, the experimental error is 0.0002 per cent absolute. However, samples are usually taken out-of-doors and the absolute humidity of the atmosphere has such an effect that during damp or rainy weather it is practically impossible to obtain a representative sample. When the relative humidity of the atmosphere is above 50 per cent at 68° F. (20° C.) or over 3.78 grains per cubic foot, results are very apt to be higher than the actual in spite of all precautions.

REAGENTS AND APPARATUS. The reagents used are phosphoric anhydride (pentoxide) in powder form and 95 per cent sulfuric acid. The apparatus consists of sample transfer fittings, sample container, heat exchanger, and phosphorus pentoxide drying tubes. Auxiliary pieces of apparatus are a sulfuric acid bubbler, sulfuric acid scrubber, phosphorus pentoxide tower, and aspirator or other source of suction.

SAMPLE FITTINGS. Two types of fittings may be used. *A* and *B*, Figure 1, illustrate the first type, which is more readily available for occasional use. *C* illustrates the second type, which is recommended for regular use. It consists of a T connecting to the drums or cylinder valve with a union and equipped with a valve on each branch. Construct this using Prestolite Y-type valves for small cylinders.

Dry all fittings at 105° to 120° C. and use while hot. Dry the valve on the container with a blow torch or other means of heating and then connect fittings *A* or *B* to this valve without passing liquid sulfur dioxide through the fitting. Finally place the moisture tube on the rubber stopper and draw the sample. The T fitting *C* does not require a drying of the drum or cylinder valve. Merely flush this valve and the T fitting *C* through one of the Y valves and finally collect the sample in the moisture tube through the other valve.

SAMPLE CONTAINER. For large samples use a half-liter suction flask with a calibration mark at the 500-cc. point; for small samples use a special cylindrical tube of 200 cc. capacity calibrated for 100 cc. and having a tip at its base of 1 cc. capacity calibrated to 0.01 cc. at its lowest portion.

Dry the containers at 120° C. Since ordinary oven-drying leaves moisture in the air in the flask and on the surface of the

glass, final drying is by means of the preliminary run described below. Repeated analyses may be made using the same container without cleaning between runs, provided air is excluded at all times. Sample containers that have not been used for several days should be treated as wet.

Heat Exchanger. A preheater is placed between the sample container and the phosphorus pentoxide tubes to prevent cooling of the tared absorption tube. For 190-cc. or 500-cc. samples evaporated slowly, use 1 foot (30.48 cm.) of glass or brass tubing. For 500-cc. samples evaporated at the maximum rate, use a 6-foot (183-cm.) helix. The tubing need not be larger than 5 mm. inside diameter.

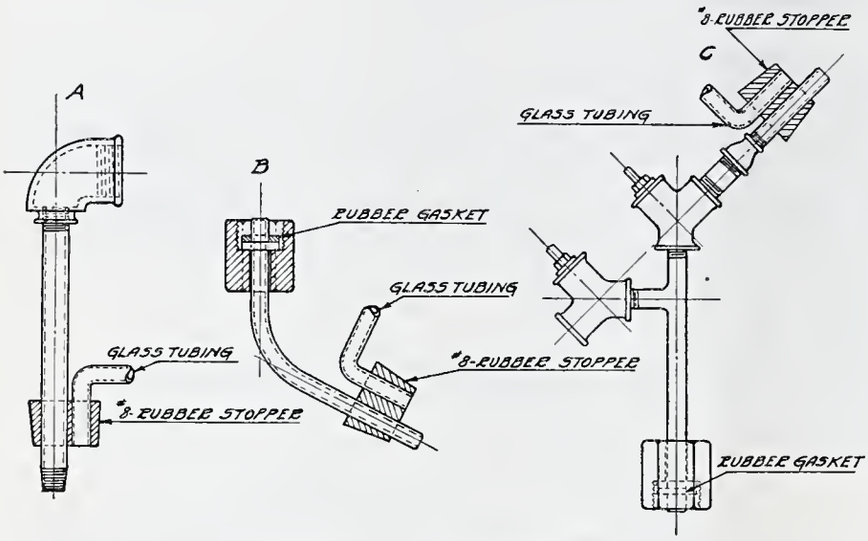

Figure 1. Sampling Tubes

The preheater is oven-dried and then finally dried in the preliminary run. Keep it closed when not in use by means of glass or wooden plugs.

Drying Tubes. Two types of drying tube may be used: the Fleming phosphorus pentoxide absorption jar (No. 3890 in A. H. Thomas catalog), or a 4-inch (10-cm.) Swartz U-tube. The Fleming jar is better adapted to 500-cc. samples because of the greater number of runs that may be made before refilling. The Swartz tube is better adapted to 100-cc. samples and throughout its life is free from channeling and has low resistance to flow of gas.

Pack the Fleming jar with a mixture prepared by shaking two parts by volume of powdered phosphorus pentoxide with one part of Gooch asbestos fiber which has been dried at 140° C. This mixture is light, porous, and has long life with minimum tendency to channel. Pack the reagent loosely in the jar on a 0.25-inch (0.6-cm.) layer of glass wool. Prepare a second phosphorus pentoxide tube like the first and place it in the absorption train. All moisture is collected in the first tube. Any change in the second tube is therefore used, with a change of sign, as a correction on the weight of the first tube. A correction for temperature, barometric pressure, and surface moisture is thus obtained automatically.

Pack the Swartz tube with glass beads coated with phosphorus pentoxide. Use beads of not more than 0.125-inch (0.3-cm.) diameter and allow them to stand in the open air for a few hours so that the moisture on the glass surfaces is in equilibrium with the air. Then place them in a stoppered bottle and add finely powdered phosphorus pentoxide in portions with shaking until the surfaces have taken up all that will stick to them. Fill the Swartz tube with these beads, using a plug of glass wool at each end.

Prepare a duplicate tube without phosphorus pentoxide to be used as a counterpoise. Weigh this tube, whether of Fleming or Swartz type, open to the air so that it is at the prevailing barometric pressure. On tests that are only run an hour, brass weights have been found to be satisfactory.

The moisture in refrigeration-grade sulfur dioxide is quantitatively removed by one phosphorus pentoxide absorption tube.

Auxiliary Apparatus. For the purpose of judging the rate of evolution of the sulfur dioxide, a sulfuric acid bubbler may be placed at the end of the train. A 15-cc. pipet cut off just below the bulb and immersed in 15 cc. of concentrated sulfuric acid in a rubber-stoppered bottle makes a safe bubbler.

The Swartz tube may be weighed after sweeping with dry air if desired. To accomplish this, sweep the tube for 3 minutes with 2 liters of air per minute. Set up a train as follows: A sulfuric acid scrubber, a phosphorus pentoxide tower, the Swartz tube, and then a manometer connected to an aspirator or other source of suction.

Sampling. Two sizes of samples may be used: the 500-cc. sample for the most accurate work, such as for 2000-lb. drums and settlement of disputes, and the 100-cc. sample for local control work and for the analysis of small cylinders when there is no disagreement. But, because of the possibilities of a larger experimental error in the case of small samples, particularly in times of high humidity, rejections should be made only on the basis of 500-cc. samples.

Flush and carefully dry the drum or cylinder valve and attach the dry fitting *A* or *B*. If fitting *C* is used, connect it directly to the drum valve and flush both drum valve and fitting through one valve of the T. Draw the sample directly from the original drum or cylinder into the especially prepared sample container used for the analysis.

The use of a small cylinder to transfer material from the original container to the laboratory is not permissible.

Preparation of Apparatus. Before starting the actual determinations, equilibrate the apparatus by collecting a full-size sample of refrigeration-grade sulfur dioxide (using the sampling connections and dried container), and evaporating it through the assembled absorption train. This is necessary to complete the drying of the sample container, to remove all air from the phosphorus pentoxide tubes, and to dry tubing connections. In transferring the sample container from the cylinder or drum to the apparatus, keep it stoppered but vented through a Bunsen valve.

At the end of the preliminary run, immediately close all stopcocks, beginning nearest the sample container, and then disconnect the absorption train. After disconnecting the sample container and the preheater tubing, close both securely.

Weigh the absorption tubes preparatory to the moisture determination. The Fleming jars must be weighed filled with sulfur dioxide. The Swartz tubes may be weighed filled with sulfur dioxide or they may be swept with air. If this is desired, sweep for 3 minutes with phosphorus pentoxide-dried air at the rate of 2 liters per minute and weigh. When weighing the absorption tubes, use a duplicate counterpoise having one end open to the

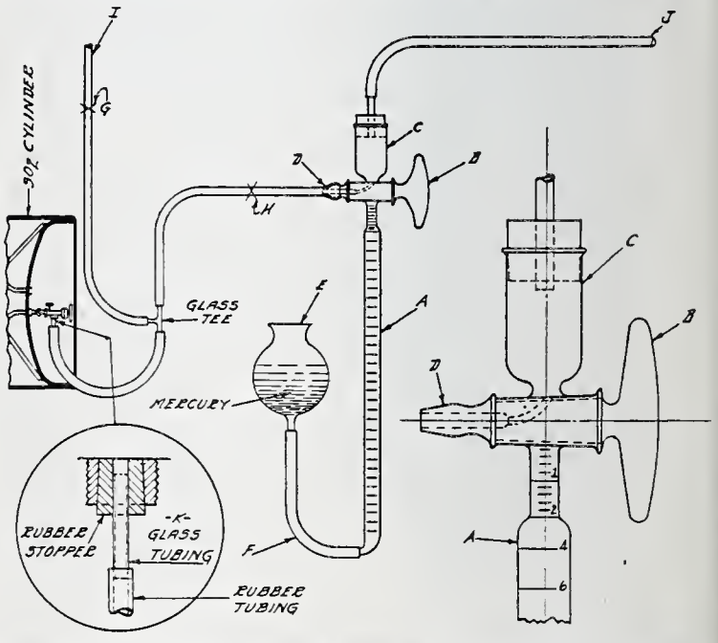

Figure 2. Apparatus for Determination of Noncondensable Gases in Liquid Sulfur Dioxide

A.	100-cc. gas buret	*E.*	Leveling bulb
B.	3-way stopcock	*F.*	Rubber tube
C.	Cup for addition of potassium hydroxide	*G, H.*	Pinchcocks
D.	Connection for sulfur dioxide inlet	*I, J.*	Open ends of rubber tubing
		K.	Glass sight tube

air. Also weigh the second Fleming jar used as a compensating tube. Equalize the pressure within all analytical phosphorus pentoxide tubes with the prevailing atmospheric pressure before closing them for weighing.

Procedure. Reassemble the absorption train. Collect the sample directly in the sample container, observing all the precautions given above, and immediately transfer it to the laboratory and connect it to the absorption train.

Regulate the rate of evaporation of the sulfur dioxide by cau-

tiously using a bath of lukewarm water. Allow at least 45 minutes for the evaporation of 100-cc. samples, and at least 1.5 hours for 500-cc. samples, when using the Swartz U-tubes. The Fleming jar requires 45 minutes for 100-cc. samples and at least 4 hours for 500-cc. samples. The rate of evaporation is limited by the back pressure of the absorption train and the danger of blowing out stoppers.

At the close of the evaporation, shut off the stopcocks in the same manner as at the end of the preliminary run and weigh the tubes, using the tare tube as counterpoise.

$$\frac{100\ M}{1.46 \times \text{cc. sample}} = \%\ \text{moisture}$$

Where 1.46 is the specific gravity of sulfur dioxide at its boiling point at atmospheric pressure, M is the gain in weight of the first phosphorus pentoxide tube less the increase or plus the decrease in the second or compensating phosphorus pentoxide tube.

Residue Test

The residue left by the evaporation of refrigeration-grade sulfur dioxide is too small for a quantitative determination to be practicable. Hence, it is determined microscopically and compared with a standard.

Procedure. Use a 200-cc. cylindrical sample container having a 1-cc. tip which at its lowest portion is graduated to 0.01 cc. Clean this container with cleaning solution, rinse with distilled water, and dry at 120° C. The glass surface should be bright and free of all film. Wipe the cylinder valve and flush. Draw a 100-cc. sample without using any sample connection. Stopper the container either with rubber stopper and Bunsen valve or with a plug of cotton wool. Evaporate to dryness and compare with standard.

Sulfuric Acid

After evaporation of the sulfur dioxide and careful removal of all sulfur dioxide vapor, as shown by iodine test, the sulfuric acid is titrated with 0.01 N caustic.

Procedure. Use a 125-cc. Erlenmeyer flask, with a calibration mark at the 100-cc. point. Clean with chromic acid cleaning solution, wash out thoroughly, and dry at 120° C. Evaporate a 100-cc. sample, using a plug of cotton wool to stopper the flask. After the evaporation, remove sulfur dioxide vapor by connecting a Gooch crucible adapter to suction and applying the rubber end to the flask, then breaking the connection. Repeat fifteen times until no odor of sulfur dioxide remains and a drop of 0.01 N iodine added to the flask is not decolorized. Prepare water for the titration by adding 2 drops of methyl red and adjusting by means of either 0.01 N sodium hydroxide or 0.01 N hydrochloric acid to the exact neutral point. Add 25 cc. of this water to the flask and titrate with 0.01 N sodium hydroxide.

$$\frac{\text{cc.} \times N \times 0.04904 \times 100}{\text{cc. of } SO_2 \times 1.46} = \%\ H_2SO_4$$

Noncondensable Gases

The 100-cc. sample of sulfur dioxide gas is collected in a 100-cc. gas buret and potassium hydroxide added. The residual gas is read as noncondensable gases.

The results for small amounts of noncondensable gases are read directly to 0.02 per cent and may be estimated to 0.005 per cent.

Reagent. 30 per cent potassium hydroxide solution.

Apparatus. The buret is similar to Eimer and Amend, No. 28940, except that it is of 100 cc. capacity and the upper tip is graduated in 0.02 cc. down to the 0.2-cc. mark.

Procedure. With pinchcock H closed, open the cock between A and C, and raise the mercury leveling bottle until the mercury just comes into the cup C. Close the stopcock B, leaving a small globule of mercury in the cup.

Place the cylinder containing the liquid sulfur dioxide on its side so that the ramshorn of the lower valve is in the liquid phase. Connect the apparatus as shown in the diagram. With the spring pinchcock G open, the cylinder valve is cautiously opened until liquid sulfur dioxide runs out at the tube and I. (Some analysts find it more convenient to substitute the use of one foot for pinchcock G.) The pinchcock H is now opened, the buret stopcock turned into the position shown in the diagram, and the pinchcock G and the cylinder valve closed. When the liquid sulfur dioxide has vaporized as indicated by the globule of mercury, the cylinder valve is opened to allow liquid sulfur dioxide to escape into the tubing only as fast as it will vaporize.

Allow the gas to sweep out the air in the apparatus, which should be accomplished in 2 or 3 minutes. With pinchcock G closed, quickly turn stopcock B so that it is open between the cylinder and the buret A, lower the leveling bulb and fill the buret with sulfur dioxide gas. Close pinchcock H and open pinchcock G. Turn stopcock B so that it is open between A and C and run this buret full of gas to waste through cup C, as it is used only to treat with any small amount of potassium hydroxide left from a previous determination. Refill the buret in the same manner as before with exactly 100 cc. of sulfur dioxide under atmospheric pressure. Close pinchcock H and turn stopcock into the position shown in the diagram. Add through cup C about 15 to 20 cc. of the potassium hydroxide solution, being careful to exclude all air. After the contraction has ceased, bring the level of the mercury in the bulb to that in the buret and read the volume of residual gas.

$$\text{cc. of residual gas} = \%\ \text{noncondensable gases in liquid phase}$$

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Note on Washing the Potassium Cobaltinitrite Precipitate

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The precipitate of potassium cobaltinitrite obtained in micromethods (*1–4*) for determining potassium becomes increasingly flocculent upon washing with water. It is therefore usually washed in centrifuge tubes by siphoning. It was found that when the precipitate is washed with a dilute solution of aluminum sulfate (1 per cent) it will be much less flocculent, so that it can be washed by the usual method of drainage after inversion. Three washings with 3 cc. of solution are usually sufficient. If the supernatant liquid from the second washing is not nearly colorless, a fourth washing should be performed.

It was also found that more consistent results can be obtained when the precipitate is to be titrated indirectly with solutions of permanganate or ceric sulfate if, upon addition of sulfuric acid and the oxidizing agent, the precipitate is thoroughly stirred for a while when the tube containing the reacting substances is placed in boiling water. Because of the instability of nitrous acid (*1*), ceric sulfate should be a better oxidizing agent for this purpose than permanganate, as it furnishes a positive ion to oxidize a negative ion.

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Quantitative Determination of Small Amounts of Hydrocyanic Acid

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THE most commonly used methods (*1*) for the determination of hydrocyanic acid have the objection that they are not quantitative for very small amounts. The method outlined below affords a means by simple technic of determining hydrocyanic acid quantitatively in exceedingly small amounts, the delicacy being measured by the amount of ammonia which can be determined by Nessler's reagent—namely, one part in one hundred million.

Hydrocyanic acid, known also as formonitrile, is subject to the general characteristic reactions of alkyl nitriles—namely, hydrolysis with either alkali or acid to form the alkyl acids or their salts and ammonia or its salts. These reactions, where R is the alkyl group, are:

$$RCN + HCl + 2H_2O \longrightarrow RCOOH + NH_4Cl$$
$$RCN + KOH + 2H_2O \longrightarrow RCOOK + NH_4OH$$

and for hydrocyanic acid:

$$HCN + HCl + 2H_2O \longrightarrow HCOOH + NH_4Cl$$
$$HCN + KOH + 2H_2O \longrightarrow HCOOK + NH_4OH$$

It is evident from the above reactions that the hydrolysis of hydrocyanic acid must be carried out in a closed system; for hydrocyanic acid would be volatilized with acid hydrolysis, and ammonia with alkali hydrolysis.

In the industrial manufacture (*4*) of ammonia and formates a mixture of cyanides (KCN + NaCN) is autoclaved with 5 to 10 parts of water for 20 to 30 minutes between 180° and 190° C. In a series of laboratory experiments samples containing standard aqueous potassium cyanide solutions equivalent to 0.01, 0.10, and 1.0 mg. of hydrocyanic acid were autoclaved for 30 minutes between 180° and 190° C. and when Nesslerized checked with equivalent ammonium chloride solutions. The hydrolysis of the potassium cyanide solution is due to the alkaline reaction of this salt. This method has two disadvantages, the caustic action on the glass autoclave and high temperature. The optimum conditions for hydrolysis, as experimentally deduced, were obtained by autoclaving for 30 minutes between 140° and 150° C. in an acid solution.

The glass autoclave is the Leiboff urea apparatus (*3*) for the determination of urea in blood. This apparatus is essentially a brass stand with a thermometer in the hollow of the rod and a circular brass plate containing six grooves from which are suspended the six glass autoclaves. The stand with the suspended autoclaves is set in an oil bath. The glass autoclave, of approximately 35 cc. capacity, is made gas-tight by a ground-glass rod which seals at the neck when the rod is so suspended. Lacking the Leiboff urea apparatus, satisfactory results could be obtained with ordinary medicinal ampoules.

PROCEDURE

Distil the hydrocyanic acid in the usual manner from a solution acidified with tartaric acid and collect the distillate into 10 cc. of 0.1 *N* sodium hydroxide. Transfer the distillate, approximately 25 cc., to the autoclave and add 5 cc. concentrated C. P. hydrochloric acid. Heat slowly in the oil bath and maintain the temperature between 140° and 150° C. for 30 minutes. After cooling, empty and rinse with distilled water into a 50-cc. beaker. Evaporate slowly on a hot plate almost to dryness to get rid of the excess acid. Dilute with distilled water, transfer to a Nessler tube, and add 5 cc. of Nessler's reagent (*2*). Compare the resulting color with a series of standard ammonium chloride solutions and calculate the parts per million of the cyanide or hydrocyanic acid present in the sample. When the ampoule is used as the autoclave, cool in an ice bath before the addition of the hydrochloric acid and then immediately seal the ampoule.

EXPERIMENTAL DATA

Solutions containing 1, 2, 3, 4, and 5 cc. of concentrated C. P. hydrochloric acid, 5 cc. of standard potassium cyanide solution (1 cc. equivalent to 0.1 mg. of hydrocyanic acid), and 20 cc. of distilled water were autoclaved for 30 minutes between 140° and 150° C. Hydrolysis was not complete when 1, 2, and 3 cc. of acid were used, whereas 4 and 5 cc. of acid showed complete hydrolysis and the ammonia evolved checked quantitatively with equivalent standard ammonium chloride solutions.

Autoclaving 5 cc. of standard potassium cyanide solutions with 5 cc. of concentrated C. P. hydrochloric acid and 20 cc. of water at 100° and 105° C. for 30 minutes showed that the liberation of ammonia was not quantitative, although more was formed at the higher temperature. Complete hydrolysis was obtained between 140° and 150° C. when autoclaved for 30 minutes.

Solutions containing 5 cc. of standard potassium cyanide, 5 cc. of concentrated C. P. hydrochloric acid, and 10 cc. of 0.1 *N* sodium hydroxide were autoclaved for 30 minutes between 140° and 150° C. Some of these solutions were Nesslerized directly with 5 cc. of Nessler's reagent, but the acidity was too great for the development of the characteristic brownish yellow color. In the others, the excess acid was neutralized with sodium hydroxide before Nesslerization. In these cases a turbidity formed due to impurities in the alkali, such as magnesium, calcium, and aluminum. However, when the excess acid was evaporated and the solution then diluted and Nesslerized, the resulting color was clear and checked quantitatively with ammonium chloride standards. For 5 cc. of the Nessler's reagent, the acid content of the solution must not exceed 0.4 cc. of concentrated hydrochloric acid.

Samples containing 5, 10, 15, 20, and 25 cc. of the standard potassium cyanide solutions were autoclaved in the usual manner with 5 cc. of concentrated C. P. hydrochloric acid and 10 cc. of 0.1 *N* sodium hydroxide. Upon subsequent removal of excess acid and Nesslerization, the characteristic brownish yellow color developed and ranged from a clear light comparable color to the brownish yellow precipitate of the iodide of Millon base, $NH_2 \cdot HgO \cdot HgI$. It is necessary, therefore, when the solution to be Nesslerized contains ammonia derived from more than 0.5 mg. of hydrocyanic acid, to take an aliquot portion for colorimetric comparison.

A one-gram sample of powder collected from a copper coil of a gas heater contained, as determined by this method, a cyanide equivalent to 75 parts per million hydrocyanic acid. This sample proved to be interesting, for Nesslerization resulted in a turbid solution which proved to be due to iron carbonyl, which, present in the original sample, distilled over with the hydrocyanic acid. The iron carbonyl was precipitated as iron hydroxide by boiling the alkali solution containing the carbonyl and the cyanide. The filtrate was autoclaved in the usual manner, and when Nesslerized a clear solution resulted.

ACKNOWLEDGMENT

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Determination of Dextrin, Maltose, and Dextrose in Corn Sirup

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An addition in procedure is applied to the method of moisture determination by distillation with toluene, as proposed by Bidwell and Sterling and modified by Rice, to make it applicable to corn sirup. A new method for the direct determination of dextrin in corn sirup is proposed. Based on the method of direct determination of dextrin, a procedure for the complete analysis of corn sirup is presented, which allows two check equations—purity and specific rotation. Analyses of several brands of confectioners' corn sirup are made.

CORN sirup (glucose, or "glue" as it is called colloquially by the candy manufacturer) has become an indispensable part of the manufacture of confectionery. One billion one hundred forty million pounds were refined in 1929, with a value of 34 million dollars. It is produced by the acid hydroylsis of corn starch under a pressure of approximately 40 pounds, in three different purities—low, regular, and high. "Purity" is defined within the industry as the amount of reducing sugars expressed as dextrose, on a dry substance basis. The "regular" purity of 43 to 44 forms the bulk of the commercial production.

Corn sirup is a thick, colorless solution of the three carbohydrates—dextrin, maltose, and dextrose. The gravity of the sirup will run from 41° to 46° Bé. (1° Bé. being expressed at 100° F.). Sirups with a gravity of 41° and 42° Bé. are more often called "mixing sirups," and are used by manufacturers of mixed table sirups. Confectioners' sirup runs from 43° to 46° Bé., the bulk being sold at 43° Bé., as this gravity represents the high practical limit at which this heavy, viscous sirup may be handled economically.

Although there are many published analyses for corn sirups or starch hydrolytic products, few are applicable to the commercial product, because the sirups used for analysis have been prepared by boiling starch in open vessels, with acids different from those used in the commercial process. Further, most workers employ a low concentration of starch suspension, whereas in the industry it is customary to use a suspension from 22° to 26° Bé., the latter figure representing the practical limit for pumping suspended starch. It is well known in the industry that the maximum purity attainable in manufacture is affected by the concentration of the starch suspension used, and it is reasonable to assume that the ratio of the various carbohydrate constituents might be altered by these same concentration differences of the starch.

Many methods have been proposed for the analysis of corn sirup. All make use of several algebraic equations obtained from laboratory determinations, such as specific rotation, reducing power before and after acid inversion, etc. Almost all employ the solids equation obtained from the moisture determination. The methods may be roughly grouped as follows:

1. Algebraic solution from solids, specific rotation, and reducing sugar equations.
2. Precipitation of the dextrin by alcohol and solution by algebraic equations.
3. Fermentation methods.
4. Destruction of the sugars, followed by polariscopic determination of the dextrin, and then algebraic solution.

Algebraic solution for three carbohydrates requires three equations, and the following are easily available in the laboratory:

$$x + y + z = \text{solids}$$
$$196x + 138.5y + 52.7z = \text{specific rotation}$$
$$1.1111x + 1.0555y + z = \text{reducing sugars as dextrose after acid hydrolysis}$$
$$0.606y + z = \text{purity or reducing sugars as dextrose on original sirup}$$

It would seem, since dextrin has no reducing power, as shown by the last equation, that the solution for the three carbohydrates would be simple, but the experience of the present authors and that of others (*4*) has been that small experimental errors are enormously multiplied, so that the final results, even in simple mixtures such as corn sirup, can be regarded only as approximate.

Recognition of this difficulty has stimulated other investigators to the direct determination of dextrin by precipitation by alcohol or a similar chemical, in which dextrin is insoluble but maltose and dextrose are soluble. Keener (*5*) stated that the precipitation of dextrin by alcohol was a most promising method but that it required further study. Experience in this laboratory has been that precipitation by alcohol is not only a disagreeable determination from an analytical standpoint, but that it also gives unreliable results, as shown in Table I.

TABLE I. DATA ON PRECIPITATION OF DEXTRIN BY ALCOHOL

Weight corn sirup, grams	5.0	5.0	5.0	5.0	5.0
Water in corn sirup, ml.	0.9	0.9	0.9	0.9	0.9
Water added, ml.	9.1	20.1	31.1	41.1	52.1
95% alcohol added, ml.	190	179	168	158	147
Final alcohol (calcd.), %	90	85	80	75	70
Dextrin found, %	19.8	13.9	8.0	4.0	1.4

The determination of the carbohydrate content by fermentation has been tried by a number of investigators. An extensive paper by Wesener and Teller (*11*) in 1916 gave the carbohydrate composition of two commercial corn sirups by this method as:

	A	B
	%	%
Dextrin	56.4	58.7
Maltose	28.8	20.2
Dextrose	14.8	21.1

Among the more recent publications on the analysis of starch hydrolytic products by fermentation separation is the paper by Nanji and Beazeley (*9*), who used two special yeasts—Saaz and Frohberg. In addition they have compared the results by their method with those obtained by the methods of Allen (*1*) and Ling (*7*) on the same starch hydrolytic products. The results have been tabulated for the usual range of specific rotation of regular-purity commercial corn sirup (Table II).

Table II. Analysis of Starch Hydrolytic Products by Fermentation

Observer:	Nanji and Beazeley		Allen		Ling	
Sp. rotation:	140	145	140	145	140	145
	%	%	%	%	%	%
Dextrin	50	54	35	38	22.5	24.5
Maltose	30	28	43	43	64.0	66.5
Dextrose	20	18	22	19	13.5	9.0
Calcd. purity	38	35	48	45	52	49

Using the factor of 0.606 for maltose (*6*), the purity has been calculated according to the analysis by each method. None agrees with the usual purity for commercial corn sirup; of the three methods, that of Nanji and Beazeley gives data farthest from that observed in commercial products.

The methods of estimating sugars by difference in polarization, before and after fermentation, give at best only a fair approximation. The methods are long, requiring from 1 to 17 days (*8*), and call for special attention to pure cultures, sterilization, and nutrition; it would be difficult to employ such methods of analysis in a commercial laboratory. Incomplete fermentation and the formation of actively optive by-products are dangers which must be constantly watched.

The destruction of the optical activity of the reducing sugars by means of Knapp's solution was first employed by Wiley (*12*). The method calls for determination of the residual polarization which is attributed to dextrin. The success of the method depends upon the inertness of the dextrin during the destruction of the maltose and dextrose.

The reliability of any analytical procedure should be tried by making a mixture of the known carbohydrates and then running a check analysis. Unfortunately, it is impossible to do this in the case of corn sirup, on account of the dextrin, and this difficulty undoubtedly accounts for the lack of satisfactory data on the composition of corn sirup. However, any set of values obtained for dextrin, maltose, and dextrose should solve in the two equations on which laboratory data can be collected, with a minimum of error:

$$196x + 138.5y + 52.7z = \text{specific rotation}$$
$$0.606y + z = \text{purity}$$

In the method of analysis which has been developed here, the purity has been reserved as a check equation after the determination of a set of values which solve in the specific rotation equation.

Direct Determination of Dextrin

Assuming a specific rotation for dextrin of 196 (*3*), one gram per 100 ml. will have an angular rotation of 3.92°. If this gram of dextrin is converted to maltose by malt and then made to 100 ml. as before, the angular rotation will be 1.0555 × 2.770° = 2.92°, or the change of one gram of dextrin to maltose per 100 ml. will cause a drop in rotation of 1.00°. Thus the drop in angular rotation will give directly the amount of dextrin, if the total final volumes of solution are the same in each case.

A blank must be run on the malt extract used, and it has been found that, if a cold water extract is made of diastatic malt, the correction from this source will be small, and yet the conversion to maltose proceeds satisfactorily. The success of the method, however, depends upon the completeness of the transformation of dextrin to maltose. Using an ordinary grade of malt, the time necessary to effect a complete conversion has been found to be 8 hours, although this time element should be determined for each source of malt. Table III gives the data obtained.

Table III. Time Necessary to Effect Complete Saccharification

Malt per Gram Corn Sirup	Time at 145° F. (62.8° C.)	Angular Rotation: Original	After saccharification	Malt blank	Corrected	Net decrease or dextrin
Gram	*Hours*		*Degrees*			%
0.20	4	23.40	21.29	0.19	21.10	2.30
0.20	4	23.40	21.33	0.19	21.14	2.26
0.20	6	23.40	21.34	0.20	21.14	2.26
0.40	4	23.40	21.49	0.38	21.11	2.29
0.40	6	23.40	21.31	0.38	20.93	2.47
0.40	6	23.40	21.27	0.34	20.93	2.47
0.40	7	23.40	21.20	0.34	20.86	2.54
0.40	8	23.40	21.21	0.36	20.85	2.55

Continuing with the same grade of malt, the concentration necessary to effect complete saccharification has been found to be 1.5 grams per gram of corn sirup, as shown in Table IV.

Table IV. Concentration Necessary to Effect Complete Saccharification

Malt per Gram Corn Sirup	Angular Rotation: Original	After saccharification	Malt blank	Corrected	Net decrease or dextrin
Grams		*Degrees*			%
0.40	18.05	17.58	0.39	17.19	0.86
1.50	18.05	17.65	0.70	16.95	1.10
1.50	18.05	17.62	0.67	16.95	1.10
2.00	18.05	18.00	1.07	16.93	1.12
2.00	18.05	17.84	0.89	16.95	1.10
2.50	18.05	18.05	1.11	16.94	1.11

The success of the method depends upon the completeness of the saccharification of the dextrin by the malt, which was tested in the following manner:

Alcohol was added to malted solution containing the equivalent of 5 grams of the original sirup in such proportions that the resulting solution was approximately 400 ml. and the concentration of alcohol 90 per cent. The opalescent solution was allowed to stand overnight and was filtered through a large amount of asbestos contained in a Gooch crucible. The precipitate was washed with a small quantity of 90 per cent alcohol, after which it was dissolved in distilled water and filtered. The clear filtrate was concentrated to the same volume as that of the original sirup, the same quantity of alcohol was added as before, and the precipitate was again obtained on the asbestos, this time in a weighed Gooch crucible. After washing, the dextrin was dried in an air oven at 105° C. to constant weight.

A blank was run concurrently on the corresponding amounts of maltose, dextrose, and ash found in the 5 grams of corn sirup, and the malt extract used for saccharification of the dextrin. These amounts were determined as follows:

Maltose. The amount of C. P. maltose taken was equivalent to the amount of maltose normally present and that obtained from saccharification of the dextrin, as determined from a preliminary analysis, in 5 grams of the corn sirup.

Dextrose. The amount of C. P. dextrose taken was equivalent to the amount present as determined by a preliminary analysis in 5 grams of sirup.

Ash. The ash added was that obtained on ashing 5 grams of the sirup.

Malt extract. The malt extract used was that of the blank in the polariscopic examination, and in an amount equivalent to that taken for 5 grams of corn sirup.

These four materials were dissolved in distilled water in such proportions that the total volume was equivalent to that of the 5 grams of sirup above; followed by the same quantity of alcohol

so as to effect a 90 per cent solution. The resulting precipitate was filtered, redissolved, reprecipitated, and weighed as described above.

The precipitation by alcohol is not a satisfactory analytical procedure, as the amount of liquid handled is large and the amount of precipitate very small. The material often sticks to the sides of the beaker, necessitating great care, as the net amount of precipitate did not exceed 35 mg. per 5 grams of corn sirup.

The results of a number of tests on sirups of different purities showed that the amount of residual unmalted dextrin would not exceed 2 per cent of that malted. Typical data obtained are found in Table V.

Table V. Data on Sirups of Different Purities

Malt per gram corn sirup, grams	1.5	1.5	1.5
Corn sirup used, grams	5.000	5.000	5.000
Water in corn sirup, ml.	0.9	0.9	0.9
Water added, ml.	21.4	21.4	21.4
95% alcohol added, ml.	415	415	415
Final concn. of alcohol, %	90	90	90
Weight of ppt. obtained, gram	0.080	0.070	0.065
Weight of ppt. from blank, gram	0.060	0.035	0.035
Net weight of dextrin, gram	0.020	0.035	0.030
Unmalted dextrin, based on sirup used, %	0.4	0.7	0.6
Unmalted dextrin, based on malted dextrin, %	1.5	2.2	1.9

Equations for Maltose and Dextrose Solution

Having determined the dextrin directly according to the malt saccharification method, solution for maltose and dextrose is made from the following equations:

I. Carbohydrate solids:

$$x + y + z = \text{carbohydrate solids}$$
$$y + z = \text{carbohydrate solids} - \text{dextrin}$$

II. Angular rotation:

$$3.92x + 2.770y + 1.054z = \text{angular rotation}$$
$$2.770y + 1.054z = \text{angular rotation} - (3.92 \times \text{dextrin})$$

Test Equation

The value obtained for dextrin, maltose, and dextrose must solve in the following two equations:

III. Specific rotation:

$$196x + 138.5y + 52.7z = \text{specific rotation} \times \text{carbohydrate solids}$$

IV. Purity equation:

$$0.606y + z = \text{reducing sugars as dextrose}$$

Analysis of Corn Sirup

Moisture. The moisture has been determined by distillation with toluene in apparatus with ground-glass connections as described by Bidwell and Sterling (*2*) and employing the modification suggested by Rice (*10*) for sugar sirups. The technic has been further improved to make it more applicable to heavy corn sirups, which tend to cake into a hardened mass, necessitating an unusually long distillation to assure complete removal of water.

Approximately 10 grams of dry Filter-Cel are run into the dry 250-ml. Erlenmeyer flask, and the weight is obtained. Then approximately 20 to 25 grams of corn sirup are run into the flask on the Filter-Cel and reweighed to find the exact weight of sirup taken. Approximately 10 grams more of Filter-Cel are added; a small dry test tube (0.5 × 4 inches, or 1.27 × 10.2 cm.) is introduced by means of a pencil, the rubber eraser end being in the test tube. Using the test tube pencil as a stirring rod, the corn sirup and the Filter-Cel are mixed together. The pencil is then removed, leaving the test tube in the flask. Approximately 75 ml. of toluene are added, the flask is connected to the receiver and condenser, the receiver is filled with toluene, and the distillation is started. An oil or glycerol bath is used, maintaining a temperature of 260° F. (126.7° C.).

Accurate results can be obtained with the Bidwell-Sterling method only by the above technic in which the corn sirup is mixed with the Filter-Cel. Otherwise the heavy sirup, with its high dextrin content, forms a compact mass, occluding moisture, and resulting in a determination in which small amounts of moisture continue to come over for more than 8 hours. Mixing the sirup with the Filter-Cel enables the determination to be completed within 6 hours, and gives higher moisture values than those obtained without mixing the sirup with the Filter-Cel. Of all the methods used for determining the moisture in corn products, the authors consider the above the most reliable and accurate for corn sugar and corn sirup.

Protein. Ten grams of corn sirup are taken for the usual Kjeldahl determination.

Ash. Ten grams in a 3-inch (7.6-cm.) silica dish are slowly carbonized with a gas flame, after which the material is ashed at a dull red heat in a muffle furnace.

Purity. The purity, or the reducing sugars calculated as dextrose, in practice is determined on the refinery converter liquor, using the Brix solids for the dry substance. As the actual solids are less than the Brix solids, the true purity will always be higher. If the carbohydrate solids are taken instead of the total solids, the purity will be increased by an additional small amount.

The purity in this investigation has been determined as follows:

A definite weight of corn sirup (approximately 10 grams of regular purity) is taken, such that when diluted to 500 ml., 12 to 15 ml. of this solution will be required to titrate 25 ml. of Fehling's solution according to the titration method of Lane and Eynon. The Fehling's solution is standardized against a one per cent solution of c. p. dextrose, and so adjusted that 25 ml. require 12.02 ml. of the dextrose solution. Under these conditions 0.1 ml. variation in titration corresponds to 0.3 to 0.4 in the purity.

In calculating the purity from the maltose and dextrose values obtained by analysis, the present authors have used the factor of 0.606 as determined by Lane and Eynon by the titration method for the usual range of titrations as employed in the determination of purities.

Table VI. Analysis of Corn Sirups

	Low-Purity Sirup[a]	Regular-Purity Sirup	High-Purity Sirup
Total solids, %	78.40	79.20	79.79
Ash, %	0.44	0.24	0.32
Crude protein, %	0.05	0.04	0.06
Carbohydrate solids, %	77.91	78.92	79.41
Purity,[b]	36.36	46.11	54.35
Specific rotation	157.9	143.4	129.3
Angular rotation:			
Original	24.60°	22.63°	20.54°
After saccharification	21.45°	20.46°	19.02°
Malt blank	0.78°	0.65°	0.67°
Corrected	20.67°	19.81°	18.35°
Dextrin by difference, grams	3.93	2.82	2.19
Maltose, grams	2.986	3.631	3.435
Dextrose, grams	0.875	1.441	2.316
Dextrin,[b] %	50.45	35.73	27.58
Maltose,[b] %	38.32	46.01	43.26
Dextrose,[b] %	11.23	18.26	29.16
Purity, calcd.	34.45	46.14	55.25
Obsvd. difference	−1.91	0.03	0.90

[a] The concentrated low-purity sirup was milky and opaque. Iodine produced a reddish coloration. When diluted to 10 grams per 100 ml., the solution was clear, and angular rotation was easily determined. The reading, however, had a slight drift downward, and it was necessary to hold the solution in a water bath for 8 hours to assure an equilibrium.
[b] Carbohydrate solids basis.

Angular Rotation. Exactly 25 grams of corn sirup are dissolved in 250 ml. of distilled water, and the angular rotation determined in the usual manner. The determination was made on duplicate samples of corn sirup, and at least two sets of readings were obtained on each sample by refilling the observation tube. From the angular rotation and the carbohydrate solids, the specific rotation can be calculated.

Dextrin. Exactly 25 grams of corn sirup are weighed in a nickel scoop. Twenty milliliters of malt solution are added to the corn sirup and thoroughly mixed after warming to approximately 100° F. (37.8° C.). The contents are then run

Table VII. Analysis of Confectioners' Corn Sirups[a]

	A	B	C	D	E	F	G
Purity[b]	44.4	42.2	45.6	43.8	51.7	52.6	43.8
Total solids, %	81.43	81.43	81.42	82.01	83.22	79.74	81.41
Ash, %	0.19	0.25	0.24	0.33	0.29	0.32	0.10
Crude protein, %	0.05	0.05	0.05	0.04	0.04	0.06	0.04
Carbohydrate solids, %	81.19	81.13	81.13	81.64	82.89	79.36	81.27
Purity[c]	45.90	43.34	47.11	45.37	52.08	54.80	46.48
Sp. rotation[c]	143.4	147.8	144.2	144.0	133.2	129.9	142.7
Angular rotation:							
Original	23.30°	23.99°	23.40°	23.52°	22.08°	20.61°	23.19°
After saccharification	20.87°	21.47°	21.40°	21.14°	20.38°	19.14°	21.04°
Malt blank	0.64°	0.76°	0.70°	0.70°	0.84°	0.64°	0.76°
Corrected	20.23°	20.71°	20.70°	20.44°	19.54°	18.50°	20.28°
Dextrin,[d] grams	3.07	3.28	2.70	3.08	2.54	2.11	2.91
Maltose	3.464	3.519	4.144	3.547	3.475	3.612	3.663
Dextrose	1.585	1.314	1.269	1.537	2.274	2.214	1.554
Dextrin,[c] %	37.81	40.43	33.28	37.72	30.64	26.59	35.81
Maltose,[c] %	42.67	43.37	51.08	43.45	41.93	45.51	45.07
Dextrose,[c] %	19.52	16.20	15.64	18.83	27.43	27.90	19.12
Purity, calcd.	45.38	42.48	46.60	45.16	52.84	55.48	46.43
Observed difference	−0.52	−0.86	−0.51	−0.21	0.76	0.68	−0.05

[a] Columns A to F are analyses made on carload shipments of corn sirup of different makes; column G represents the analysis on a composite sample of corn sirup made at one factory over a period of a week.
[b] Brix solids basis.
[c] Carbohydrate solids basis.
[d] By difference.

into a 150-ml. extraction flask. The nickel scoop is washed with another 20-ml. portion of malt solution, which is added to the contents already in the extraction flask. The washing is continued with another 10-ml. portion of malt solution, making 50 ml. in all, and followed with a final wash of 10 ml. of distilled water. The determination is run in duplicate; 50 ml. of malt solution are run into another flask, and the three flasks placed in a water bath, at 145° to 148° F. (62.8° to 64.4° C.) for 8 hours.

At the end of this period the three flasks are removed and placed on a steam bath for at least 30 minutes to thoroughly coagulate the protein. The flasks are then placed in a water bath, cooled, and contents filtered. The two samples of corn sirup are made to 250 ml., and the malt to 100 ml. The angular rotation is determined in the usual manner. Two-fifths of the observed reading for the malt solution is the blank which must be subtracted from the sirup reading to obtain the net reduction in angular rotation. As described above, the net reduction in angular rotation is the weight of dextrin in 10 grams of corn sirup.

Preparation of Malt Solution. Distillers' malt (187.5 grams) is ground and run into a flask, and enough cold distilled water added to cover the malt. The flask is then placed in a water bath at approximately 60° F. (15.6° C.) for one hour. At the end of this period, the flask contents are poured into a filter, and the filtrate is returned until clear. It is then allowed to run into a 250-ml. volumetric flask, and cold distilled water is added to the material in the filter as needed until approximately 250 ml. have been obtained. The malt solution is then made to 250 ml. and used as directed above.

To check the method which has been proposed, three corn sirups covering a wide range of purity were supplied by another refinery and analyzed. The results are found in Table VI.

The data indicate that the formation of maltose passes through a maximum value, as previous investigators have reported. The percentages of the three carbohydrates, however, differ.

Following the above determinations, samples of confectioners' corn sirup as supplied to the trade by four manufacturers were analyzed. The data are given in Table VII.

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International Atomic Weights 1933

In response to requests, we reprint here from the *Journal of the American Chemical Society* for February, 1933, the 1933 report of the Committee on Atomic Weights of the International Union of Chemistry.

	Symbol	At. No.	Atomic Weight		Symbol	At. No.	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.93	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.8
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.10
Carbon	C	6	12.00	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Radium	Ra	88	225.97
Cesium	Cs	55	132.81	Radon	Rn	86	222
Chlorine	Cl	17	35.457	Rhenium	Re	75	186.31
Chromium	Cr	24	52.01	Rhodium	Rh	45	102.91
Cobalt	Co	27	58.94	Rubidium	Rb	37	85.44
Columbium	Cb	41	93.3	Ruthenium	Ru	44	101.7
Copper	Cu	29	63.57	Samarium	Sm	62	150.43
Dysprosium	Dy	66	162.46	Scandium	Sc	21	45.10
Erbium	Er	68	167.64	Selenium	Se	34	79.2
Europium	Eu	63	152.0	Silicon	Si	14	28.06
Fluorine	F	9	19.00	Silver	Ag	47	107.880
Gadolinium	Gd	64	157.3	Sodium	Na	11	22.997
Gallium	Ga	31	69.72	Strontium	Sr	38	87.63
Germanium	Ge	32	72.60	Sulfur	S	16	32.06
Gold	Au	79	197.2	Tantalum	Ta	73	181.4
Hafnium	Hf	72	178.6	Tellurium	Te	52	127.5
Helium	He	2	4.002	Terbium	Tb	65	159.2
Holmium	Ho	67	163.5	Thallium	Tl	81	204.39
Hydrogen	H	1	1.0078	Thorium	Th	90	232.12
Indium	In	49	114.8	Thulium	Tm	69	169.4
Iodine	I	53	126.92	Tin	Sn	50	118.70
Iridium	Ir	77	193.1	Titanium	Ti	22	47.90
Iron	Fe	26	55.84	Tungsten	W	74	184.0
Krypton	Kr	36	83.7	Uranium	U	92	238.14
Lanthanum	La	57	138.92	Vanadium	V	23	50.95
Lead	Pb	82	207.22	Xenon	Xe	54	131.3
Lithium	Li	3	6.940	Ytterbium	Yb	70	173.5
Lutecium	Lu	71	175.0	Yttrium	Y	39	88.92
Magnesium	Mg	12	24.32	Zinc	Zn	30	65.38
Manganese	Mn	25	54.93	Zirconium	Zr	40	91.22
Mercury	Hg	80	200.61				

Determination of Sulfur and Chlorine in Gasoline

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A laboratory method has been developed for the determination of chlorine and sulfur in gasolines. The procedure is simple and does not demand any unusual apparatus or special technic.

Excellent results are obtained upon gasolines containing added quantities of several types of chlorohydrocarbons in the presence of various quantities of sulfur compounds. A variation in the type of chlorine compound present in the gasoline does not affect the accuracy of the determination.

A comparison of this procedure with a modification of the oxygen bomb method to include the determination of chlorine yields concordant results.

Various methods of treating gasoline through the use of chlorides or other soluble salts of zinc, mercury, iron, copper, and other metals allow the possible chlorination of some of the hydrocarbons. A determination of sulfur in the treated products by the A. S. T. M. lamp method (D-90-26T) will result in an acidity in excess of that due to the sulfur content, as the chlorine will go over as hydrogen chloride alone. The apparent sulfur will therefore be in excess of the actual sulfur value. Under such circumstances, there is a need for a simple analytical procedure to determine the sulfur and chlorine contents of the gasoline.

Several methods (*1*, *3*, *6*, *8*) for the determination of sulfur and chlorine are available, but in general they are not adapted to rapidity and ease of manipulation in control work. The bomb methods (*3*) consist essentially of oxidizing a weighed sample in a bomb with determination of the sulfur as the sulfate and subsequent titration with silver nitrate for chlorides (A. S. T. M. method 129–27 and Parr sodium peroxide method). The method of Willard and Thompson (*8*), based upon oxidation of the sample with fuming sulfuric acid, is very satisfactory for the determination of chlorides. The halogen is distilled into alkaline arsenate and precipitated as silver halide. Metals may be determined in the same solution. The lamp method of Bowman (*1*) favors the combustion of the wick after burning the sample. This prolongs an analysis and it has been found unnecessary. The method described is adapted to illuminating oils, petroleum naphthas, gasolines, and other volatile motor fuels which can be analyzed by the A. S. T. M. method D-90-26T.

A simple and rapid procedure of analysis with a high degree of accuracy is desired. The several possible sulfur methods which suggest themselves as suitable with the necessary modifications to include chlorine are the oxygen bomb method, the sodium peroxide bomb (*4*), and the A. S. T. M. lamp determination. In each instance the resulting solution may be analyzed for sulfur and chlorine either gravimetrically or volumetrically.

The new analytical procedure consists of three steps: burning the gasoline in the standard A. S. T. M. lamp with absorption of the combustion products in sodium carbonate; determination of the total acidity due to the combustion of the sulfur and chlorine-containing hydrocarbons; and determination of the chlorine content by Mohr's procedure (*5*).

The total acidity is a measure of the sulfur trioxide and hydrochloric acid formed by combustion of the sulfur and chlorine-containing hydrocarbons and is expressed as percentage of sulfur. The chlorine content with a suitable factor as determined by titration is subtracted from the total acidity. The true sulfur percentage is obtained by difference.

Procedure

Weigh 10 to 15 cc. of the gasoline sample for analysis in an Erlenmeyer flask, fit the wicking into the flask, and burn the gasoline according to the detailed A. S. T. M. procedure. However, do not use hydrochloric acid in the titration of the unused sodium carbonate solution as is customary in the sulfur determinations, but substitute 0.0623 N sulfuric acid with methyl orange as an indicator. Remove the neutralized solution from the tower with suitable washing and filter it, if necessary, to separate any suspended carbon. Evaporate the filtered solution to approximately 25 to 35 cc. After cooling, add a few drops of a saturated potassium chromate solution. Titrate the solution with 0.1 N silver nitrate solution to the appearance of a red coloration. Dichlorofluorescein (*2*) was tried as an indicator in this titration but was not satisfactory in the presence of the methyl orange. The color change of the potassium chromate indicator is more pronounced.

The end point as obtained by the sulfuric acid titration indicates the total acidity or the acidity due to the sulfur plus that due to the chlorine content of the sample. Therefore the percentage of chlorine is given by

$$\%\ \text{chlorine} = \frac{\text{cc. } 0.100\ N\ AgNO_3 \times 100 \times 0.00355}{\text{grams sample burned}}$$

The sulfur content is obtained by difference,

$$\%\ \text{sulfur} = \%\ \text{total acidity} = \%\ \frac{\text{chlorine}}{2.22}$$

where 2.22 is the factor for converting sulfur to chlorine and total acidity is expressed in terms of percentage of sulfur.

Outline of Work

The method was tested out by obtaining data upon gasolines of known sulfur and chlorine content. The chlorine content was varied by the addition of known quantities of chlorine derivatives of hydrocarbons, chosen to include several types of chlorinated hydrocarbons. The gasolines used were a naphtha free from chlorine and extremely low in sulfur, and several cracked gasolines containing various percentages of sulfur. The chlorohydrocarbons were added to each type of gasoline in percentages to give chlorine contents as high and as low as likely to be encountered in practical work. The chlorohydrocarbons utilized were: amyl chloride, amylene dichloride, benzyl chloride, butyl chloride, carbon tetrachloride, dichlorobenzene, ethylene chloride, isopropyl chloride, isobutyl chloride, and propyl chloride. Each of these materials was of the highest purity furnished by the Eastman Kodak Company.

Table I

Chlorohydrocarbon	Chlorine Added	Total Acidity Found (Sulfur) 1	2	Chlorine Found 1	2	Error	Sulfur Found 1	2	Error
	%	%	%	%	%		%	%	
Low-sulfur and high-chlorine gasoline									
Gasoline used	...	...	...	...	...	.....	0.041	0.043	.....
Benzyl chloride	0.341	0.195	0.200	0.346	0.348	+0.006	0.039	0.043	−0.001
Butyl chloride	0.214	0.140	0.147	0.220	0.224	+0.008	0.040	0.045	+0.001
Isobutyl chloride	0.294	0.167	...	0.296	...	+0.002	0.038	...	−0.004
Propyl chloride	0.265	0.161	0.165	0.269	0.263	+0.001	0.040	0.046	+0.001
Isopropyl chloride	0.206	0.142	0.143	0.216	0.217	+0.011	0.045	0.044	+0.003
Ethylene chloride	0.244	0.157	0.154	0.251	0.257	+0.010	0.042	0.038	−0.002
Carbon tetrachloride	0.291	0.177	0.179	0.307	0.300	+0.013	0.033	0.043	−0.004
Low-sulfur and low-chlorine gasoline									
Gasoline used	...	...	...	...	...	.....	0.042	...	.....
Amylene dichloride	0.023	0.053	0.054	0.023	0.022	0.000	0.042	0.044	+0.001
Butyl chloride	0.019	0.048	0.053	0.019	0.017	−0.001	0.040	0.044	0.000
Propyl chloride	0.022	0.048	0.047	0.025	0.019	0.000	0.036	0.039	−0.004
Isopropyl chloride	0.028	0.051	0.054	0.023	0.024	−0.004	0.041	0.043	0.000
Ethylene chloride	0.039	0.060	0.061	0.035	0.036	−0.003	0.040	0.043	0.000
Carbon tetrachloride	0.059	0.064	0.061	0.064	0.056	+0.001	0.036	0.036	−0.006
High-sulfur and high-chlorine gasoline									
Gasoline used	...	...	...	...	...	.....	0.328	...	.....
n-Amyl chloride	0.090	0.356	...	0.091	...	+0.001	0.315	...	−0.013
Amylene dichloride	0.390	0.512	...	0.404	0.407	+0.016	0.329	...	+0.003
Benzyl chloride	0.258	0.443	...	0.265	...	+0.007	0.323	...	−0.005
Isobutyl chloride	0.232	0.502	...	0.238	0.236	+0.005	0.330	...	+0.002
o-Dichlorobenzene	0.130	0.386	...	0.135	...	+0.005	0.325	...	−0.003
Ethylene chloride	0.262	0.450	...	0.272	0.277	+0.013	0.327	...	−0.001
Propyl chloride	0.361	0.520	...	0.362	0.371	+0.006	0.320	...	−0.008
Isopropyl chloride	0.377	0.502	...	0.386	...	+0.009	0.326	...	−0.002
High-sulfur and low-chlorine gasoline									
Gasoline used	...	...	...	...	...	.....	0.328	...	.....
Amylene dichloride	0.033	0.338	0.344	0.033	0.035	+0.001	0.323	0.330	−0.001
Benzyl chloride	0.032	0.350	0.355	0.038	0.039	+0.006	0.330	0.329	+0.002
Isobutyl chloride	0.017	0.343	0.337	0.024	0.018	+0.004	0.332	0.331	+0.004
Ethylene chloride	0.037	0.346	...	0.038	...	+0.001	0.330	...	+0.002
Propyl chloride	0.020	0.339	0.338	0.019	0.023	+0.001	0.330	0.328	+0.001
Isopropyl chloride	0.031	0.336	...	0.028	...	−0.003	0.323	...	−0.005
Chlorine in the absence of sulfur[a]									
Benzyl chloride	0.031	...	...	0.035	0.037	+0.005	...	...	.....
Benzyl chloride	0.101	...	...	0.113	0.103	+0.007	...	...	.....
Butyl chloride	0.028	...	...	0.027	0.032	+0.002	...	...	.....
Butyl chloride	0.076	...	...	0.077	...	+0.001	...	...	.....
Butyl chloride	0.121	...	...	0.123	0.127	+0.004	...	...	.....
Ethylene chloride	0.088	...	...	0.084	0.083	−0.004	...	...	.....
Ethylene chloride	0.221	...	...	0.228	0.226	+0.011	...	...	.....
Amylene dichloride	0.037	...	...	0.038	0.039	+0.002	...	...	.....
Amylene dichloride	0.136	...	...	0.133	0.140	+0.001	...	...	.....
Amylene dichloride	0.261	...	...	0.265	...	+0.004	...	...	.....
Isobutyl chloride	0.028	...	...	0.025	0.026	−0.002	...	...	.....
Isobutyl chloride	0.173	...	...	0.177	0.180	+0.006	...	...	.....
Chlorinated cracked gasoline									
Gasoline used	...	...	...	0.040	...	.....	0.280	...	.....
Amylene dichloride	0.052	...	...	0.094 − 0.040 = 0.054		+0.002	0.275	...	−0.005
Benzyl chloride	0.080	...	...	0.122 − 0.040 = 0.082		+0.002	0.280	...	0.000
n-Butyl chloride	0.099	...	...	0.140 − 0.030 = 0.110		+0.100	0.272	...	−0.008
Ethylene chloride	0.288	...	...	0.324 − 0.040 = 0.284		+0.004	0.280	...	0.000

[a] A cleaners' naphtha containing 0.005 per cent sulfur was used.

Table II. Use of the Oxygen Bomb

Chlorohydrocarbon	Chlorine Added	Chlorine Found by Bomb	Error	Chlorine Found by Lamp	Error	Sulfur Found by Bomb	Sulfur Found by Lamp
	%	%		%		%	%
Gasoline	...	0.041	.....	0.040	.....	0.282	0.280
Ethylene chloride	0.329	0.325	−0.004	0.324	−0.001	0.280	0.280
Amylene dichloride	0.390	0.396	+0.006	0.406	+0.016	...	...
Benzyl chloride	0.341	0.345	+0.004	0.347	+0.006	...	...
Ethylene chloride	0.262	0.267	+0.005	0.264	+0.002	...	...
Isobutyl chloride	0.294	0.299	+0.005	0.296	+0.002	...	...
Isopropyl chloride	0.377	0.383	+0.006	0.386	+0.009	...	...
Benzyl chloride	0.032	0.036	+0.004	0.038	+0.006	0.325	0.329
Propyl chloride	0.020	0.018	−0.002	0.021	+0.001	0.327	0.329

Discussion of Results

The data shown in the accompanying tables cover the analyses conducted upon each "synthetic" chlorinated gasoline. In Table I the complete range of possible combinations of low and high sulfur and chlorine contents as they would probably occur in gasolines has been investigated. The errors as shown in the table are computed on the basis of the average results of each analysis.

The results show that the presence of a range of percentages of chlorine from 0.017 to 0.390 per cent does not affect the accuracy of the sulfur determination upon the samples of sulfur contents from 0.005 to 0.328 per cent. In addition, excellent checks are obtained for the chlorine contents as calculated from the quantity of chlorohydrocarbon added. The chlorine results are apparently not dependent upon the chemical structure of the chlorohydrocarbon present. In practically every determination the percentage of chlorine found is slightly higher than the quantity added, although the differences are well within the accepted limits of error of the lamp sulfur determination.

In the case of gasolines containing percentages less than 0.10 of chlorine and sulfur, 0.05 *N* or 0.01 *N* silver nitrate can be advantageously used. Best results are obtained by concentrating the solution after titration with sulfuric acid to not over 25 cc. The potassium chromate indicator should be a concentrated solution. If the acid titration is carried beyond the end point as shown by the methyl orange indicator, a few drops of sodium carbonate should be added to make the solution neutral.

The high-sulfur gasoline did not burn very readily. This is apparently due to the highly aromatic content of this

particular material. The flame yielded a "smoky" absorption solution which necessitated filtration in all cases. The samples containing isobutyl and isopropyl chlorides required much attention, smoking much more than any other samples. Regardless of the difficulties, satisfactory results were obtained.

The following analyses were made on several gasolines containing various chlorohydrocarbons by the oxygen bomb method (A. S. T. M. designation D-129-27), determining the sulfur by barium sulfate precipitation and the chlorine by titration with silver nitrate. The results were compared to those obtained on the same samples by the lamp method. Excellent check results were obtained between the two procedures.

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Determination and Occurrence of Fluorides in Sea Water

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The occurrence and determination of fluorides in sea water have received scant attention, and the data that have been obtained show marked variation. The authors have adapted the zirconium nitrate–sodium alizarin sulfonate indicator for the determination of fluorides. The chloride and sulfate ions of sea water interfered with the determination, but the difficulty is eliminated by preparation of comparison standards containing the same quantity of these ions as a sample of sea water being studied. The speed of the reaction between the zirconium alizarin lake and the fluoride ion is increased by heating, thus materially reducing the time necessary to reach equilibrium and making the determination more rapid. For ocean waters, the fluoride ion is proportionate to the chlorinity, the fluoride-chlorinity constant being 7.0 × 10⁻⁵. Surface coastal waters and other waters that are subjected to dilution appear to give a slightly higher fluoride-chlorinity ratio.

In 1850 Forchhammer (*5*) obtained 0.7 mg. of fluorine per liter of sea water collected near Copenhagen. Carnot in 1895 (*2*) in a sample of water from the Atlantic found 0.82 mg. per liter, while Carles (*1*), a few years later, reported as high as 12 mg. in water from the Basin of Archachon. Gautier and Clausmann (*6*) obtained results in the waters of the Atlantic and Mediterranean that varied between 0.240 and 0.334 mg. per liter.

Forchhammer determined the fluoride by first precipitating it as calcium fluoride. Sulfuric acid was added to the precipitate and the extent to which the liberated hydrofluoric acid etched glass was used as a measure of the amount actually present. Carles used much the same method but precipitated as barium fluoride. Carnot evaporated large quantities of water to which calcium hydroxide had been added. After washing the precipitate free of soluble salts and treating it with acetic acid to rid it of calcium carbonate, silica and sulfuric acid were added. The liberated silicon tetrafluoride was conducted through a solution of a potassium salt, and the potassium fluosilicate precipitated and weighed.

Gautier and Clausmann precipitated the fluorides as barium fluoride by the addition of barium chloride. Barium sulfate was precipitated simultaneously, retaining a portion of the fluorides. By an elaborate treatment of the precipitates in special apparatus, lead fluoride was eventually obtained and converted to colloidal lead sulfide, which was measured colorimetrically against known standards, and the amount of fluorides present deduced from the quantity of lead sulfide.

Investigation of these methods shows that a relatively large portion of the fluorides was not precipitated and was found in the filtrate. When a sample of sea water containing 1.25 mg. of fluorine was heated with barium chloride in alkaline solution, nearly half the fluoride remained in solution.

In the development of an analytical procedure, the methods of Casares and Casares (*3*) and De Boer (*4*) have been modified to meet the conditions encountered. Zirconium nitrate and sodium alizarin sulfonate react to form a brilliant reddish violet lake which is stable in acid solution. De Boer has shown that a number of metallic salts form a lake with this particular dye but only two, zirconium and hafnium, are stable in the presence of hydrochloric acid. Samples of sea water, when treated with sodium alizarin sulfonate, showed a coloration which completely disappeared upon the addition of hydrochloric acid. The stable reddish violet color produced by zirconium nitrate and sodium alizarin sulfonate in acid solution, however, is destroyed by the addition of fluorides, the pale yellow color of the alizarin sulfonate reappearing. Thus conditions may be created where various amounts of fluoride will react with the same amount of the lake under identical conditions and cause the formation of a color series ranging from a red to a yellow.

Applying the method directly to sea water, two difficulties are encountered—the effect of various salt concentrations upon the indicator and the marked slowness of the reaction—but these have been largely eliminated by modification of the method.

Method of Analysis

Preparation of Indicator. Dissolve 0.87 gram of crystalline zirconium nitrate in 100 ml. of water. Dissolve 0.17 gram of sodium alizarin sulfonate in 100 ml. of water. Mix the two solutions. Dilute 15 ml. of the resulting mixture to 100 ml. to serve as indicator.

Standard Sodium Fluoride Solution. Weigh out exactly 222 mg. of pure, dry sodium fluoride and dissolve in 1 liter of water. When 100 ml. of this solution are diluted to 1 liter, 1 ml. is equivalent to 0.01 mg. of fluorine.

Solution of Salts for Standards. Prepare a solution containing 37.9 grams of fluoride-free sodium chloride and 8.25 grams of fluoride-free $MgSO_4 \cdot 7H_2O$ per liter. This solution has a chlorinity (*7, 8*) of 23 grams of chlorine per liter and a ratio of sulfate to chloride analogous to sea water.

Preparation of Standards. In a series of 100-ml. flasks add 8, 10, 11, 12, 13, 14, 15, and 16 ml. of standard sodium fluoride solution, which will represent 0.80 to 1.60 mg. of fluorine per liter when diluted to 100 ml. The dilution is made with the salt solutions and distilled water to give a chlorinity approximately equivalent to that of the waters under investigation.

The sea waters being studied have chlorinities approximating 17 grams per liter. Thus, to prepare a standard containing the equivalent of 1.50 mg. of fluorine per liter, 15.00 ml. of the sodium fluoride solution are added to a 100-ml. flask, 74 ml. (73.91 ml.) of the salt solution added, and the whole diluted to 100 ml. with distilled water. The set of standards is accorded the same treatment as given below.

Analysis of Samples

One hundred milliliters of the samples to be analyzed and the standards are transferred to 250-ml. Erlenmeyer flasks and 2 ml. of 6 *N* hydrochloric acid added. If the chlorinity varies from 14 to 17 per mille, 2.00 ml. of the indicator solution are added. For each unit increase in chlorinity above 17 per mille, the amount of indicator used in both the samples and standards is increased by 0.10 ml., and for each unit decrease below 14 per mille the amount of indicator is decreased by 0.05 ml. After the addition of the indicator, the solutions are brought to the boiling point to facilitate the reaction between the indicator and the fluoride ions. Upon cooling, the solutions are transferred to 100-ml. Nessler tubes with minimum rinsing, adjusted to equal heights, and allowed to stand for 4 hours before making comparisons. If there is a difference between the chlorinity of the sample and the standard, a correction of 0.054 mg. of fluorine per liter for each unit of difference should be made. The correction is added if the chlorinity of the sample is less than the standard and subtracted if the chlorinity of the sample is higher. It is desirable to run samples and standards under identical conditions.

Discussion and Criticism of Method

Effect of Ions. Studies of the individual effect of the major ions of sea water showed that the presence of sulfates caused the greatest deviations; the chlorides likewise had a small effect. To compensate for this error, a solution of salts is prepared and used in making the comparison standards. It is essential that the salts utilized be recrystallized, as they are apt to contain traces of fluorides.

Investigations were conducted as to the effect upon the indicator of many ions found in relatively small concentration in sea water. In all cases, maximum concentrations of the substances, as actually exist in sea water, were used and negative results were obtained for bromide, carbonate, nitrate, calcium, barium, potassium, strontium, iodide, silicate, and phosphate ions. The ferric and ferrous ions, present to the extent of at least 1 mg., showed a slight action in distilled water solutions, but in salt solutions the effect was reduced considerably below the experimental error of the method.

Table I illustrates the effect of the salts of sea water on the fluorine determination. Four different samples of sea water having widely varying chlorinities were selected and compared with the fluorine standards containing different concentrations of the dissolved salts solution expressed as chlorinity.

Table I. Fluorine Content of Samples of Sea Water

Sample	Chlorinity of Samples	Fluorine Content Measured against Standards Containing Chlorinities of: 19‰ Cl	17‰ Cl	14‰ Cl	10‰ Cl
	‰	*Mg./l.*	*Mg./l.*	*Mg./l.*	*Mg./l.*
1	18.85	1.26	1.38	1.50	1.74
2	17.25	1.02	1.14	1.26	1.50
3	15.57	0.90	0.98	1.14	1.40
4	13.35	..	0.70	0.86	1.14

Temperature. Temperature materially affects the speed of the reaction between the lake and the fluoride ions, as the equilibrium finally established is a function of the temperature. Long standing or continual boiling affects the color and it is very desirable always to prepare standards simultaneously with the samples being analyzed.

The time required for the indicator to react with the fluoride ions at room temperatures varied from 36 to 48 hours before conditions of equilibrium were obtained. However, by causing the reaction to take place in hot solution, the time was shortened markedly. A number of determinations run at room temperature for 48 hours gave identical results on the same series of samples when the reaction was accelerated by heat, the samples cooled and compared after standing 4 hours. Conditions of equilibria exist, and after cooling to room temperature it is essential that the samples and standards be permitted to stand for at least 3 or 4 hours before making comparisons, as otherwise discrepancies will be noted. Concordant data were obtained on series of samples and standards that had been permitted to stand for one week, the results agreeing, within the experimental error, with those obtained by the regular method.

Accuracy of Determination. A maximum variation of not more than 0.05 mg. of fluorine per liter is obtained in samples containing from 1.00 to 1.60 mg. of fluorine per liter. Seven samples analyzed independently by two persons showed an average variation of 0.02 mg., exact checks being obtained on three samples, while the maximum variation of 0.05 mg. was recorded on two.

The sensitivity is a function of the concentration of indicator used, the quantity of dissolved salts, the amount of fluoride, and the concentration of the acid. The determination is more reliable when carried out in the presence of dissolved salts than when the salt concentration is reduced to a minimum. Too much acid tends to decrease the sensitiveness of the test, but the use of a strong acid (hydrochloric) is to be preferred over that of a weak acid (acetic).

Effect of Storage. Samples stored in glass bottles and analyzed periodically for two months showed no variation.

Sources of Samples Studied

Samples of water were collected at various stations and different depths in Washington Sound, the Gulf of Georgia, the Strait of Juan de Fuca, and at points from 50 to 200 miles off the coast of Washington and the west coast of Vancouver Island. A summary and mean of the results of analyses of 63 samples are given in Table II.

Table II. Results of Analyses of Samples Taken at Different Depths and Various Stations

Depth	Number of Samples	Chlorinity	Fluorine		Ratio F/Cl
Meters		‰	*Mg./l.*	*Millimols*	
Surface	10	16.66	1.19	0.0626	7.2×10^{-5}
10	9	17.07	1.17	0.0616	6.9×10^{-5}
25	9	17.40	1.21	0.0637	7.0×10^{-5}
50	8	17.76	1.23	0.0647	7.0×10^{-5}
100	6	17.90	1.22	0.0642	6.8×10^{-5}
100–500	15	18.53	1.27	0.0668	6.9×10^{-5}
500–2500	6	18.90	1.30	0.0684	6.9×10^{-5}

As the maximum error of the fluoride determination was 0.05 mg. per liter and that of the chlorinity 0.01 per mille, the maximum deviation of the fluoride-chlorinity constant would be $\pm 0.3 \times 10^{-5}$. With the exception of five individual samples, all the data from which Table II is compiled are within this range of error for the average ratio for a given depth.

During the cruise of the research boat, M. S. *Catalyst*, on which the samples were collected, two additional samples were secured from the surface at the mouth of the Fraser River. One sample had a chlorinity of 5.88 per mille, contained 0.55 mg. of fluorine, and showed a fluoride-chlorinity

ratio of 9.3×10^{-5}; the second sample had a chlorinity of 1.78 per mille, contained 0.41 mg. of fluorine, and gave a ratio of 22.0×10^{-5}. This would indicate that the diluting waters of the river had a fluoride-chlorinity ratio considerably greater than that of the sea. Further investigation with river water and the diluted sea water at the mouths of rivers is contemplated, following a further study for detecting smaller amounts of fluoride by the method described above.

From October, 1931, to July, 1932, samples were collected about once a week at the surface from the observation platform at the field laboratories of the Oceanographic Laboratories of the University of Washington, at Friday Harbor, Wash. Thirty analyses showed an average chlorinity of 17.00 per mille with an extreme variation from 16.46 to 17.39 per mille; an average fluoride content of 1.24 mg. of fluorine per liter with a variation from 1.17 to 1.32 mg. of fluorine; and a fluoride-chlorinity ratio of 7.3×10^{-5}. Only one sample showed a variation greater than the calculated experimental error.

Discussion of Results

Approximately 100 different samples have been analyzed for fluoride, and an average fluoride-chlorinity ratio of 7.0×10^{-5} was obtained.

Comparing the data given above for 30 samples of surface waters with Table II, waters from the surface appear to have a slightly greater fluoride-chlorinity ratio. Of the samples discussed in Table II, 41 were secured in the open ocean. The average ratio of these 41 samples (for all depths) was 6.85×10^{-5}, while that for "inside" waters (straits, sounds, bays, and inlets) was 7.18×10^{-5}. The maximum values for ocean waters were obtained in the surface samples and were never higher than 7.2×10^{-5}, while the maximum values of inside waters were 7.5×10^{-5}. The minimum ratio for the inside waters was obtained in the deep samples and more nearly approached the ratio for ocean waters. The average chlorinity for all the ocean waters was 18.23 per mille and that for the inside waters 17.16 per mille, or a difference of about 1 per mille.

Assuming that an ocean water of 18 per mille chlorinity and average fluorine-chlorinity ratio is diluted by river water to 17 per mille, calculations show that the concentration of fluorine in the diluting water may vary from 0.15 to 1.2 mg., depending upon the value used for the experimental error. As the average river water has a chloride content of from 2 to 6 mg. of chlorine per liter, the fluoride-chlorinity ratio for fresh waters is many times greater and thus accounts for the very slight variations noted for inside waters and some surface ocean waters.

Conclusions

The zirconium nitrate–sodium alizarin sulfate method has been modified and is applicable for the analysis of sea water.

The fluoride concentration of sea water is a function of the dissolved salts or chlorinity and ranges from 1.0 to 1.4 mg. of fluorine per liter. It shows no seasonal fluctuations, but increases with depth until approximately uniform conditions of salinity or chlorinity are encountered.

The fluoride concentration is proportional to the chlorinity and the fluoride-chlorinity ratio is 7.0×10^{-5}. This ratio is slightly higher for surface coastal waters and for some waters of straits, channels, and estuaries.

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Removal of Corrosion Products from Iron

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CORROSION tests are usually made by subjecting the test specimens to the corrosive medium under the desired conditions and after a period of time removing the adherent corrosion products and determining the loss in weight of the specimens.

In order to test different means of removing the corrosion deposits, several pieces of Bessemer wire were corroded and the corrosion products removed by four methods. The efficiency of each method in stripping the deposit from the metal was observed, and also whether or not the iron itself was attacked.

Pieces of iron wire 4 to 5 cm. in length were pickled in sulfuric acid and inhibitor in order to remove any oxide coating, and then washed, dried, measured, and weighed. They were placed in a large desiccator over dilute hydrochloric acid and allowed to remain there for 144 hours. The cover of the desiccator was arranged to allow free circulation of air and the wires were well out of contact with the dilute acid. This atmosphere was highly corrosive and at the end of the time period the specimens were covered with a deposit which consisted of red rust and black oxide of iron. They were then cleaned according to several methods and the losses in weight were found. As all the samples which were cleaned by any one method had been in the corrosive atmosphere for the same length of time, it was assumed that about the same amount of corrosion would be experienced by each specimen, and that they would be checks on each other.

The following methods were used to remove the corrosion products:

1. Brushing with a wire bristle brush.
2. Pickling with sulfuric acid containing an inhibitor.
3. Pickling with ammoniacal ammonium citrate.
4. Pickling with sodium hydroxide and zinc.

The first three methods have been in use for many years. The fourth was recently described by Cournot and Chaussain (*1*).

Removal of Corrosion Products

A number of wires were removed from the container at the same time and brushed by hand with a wire brush, alternating the brushings with washing under a stream of water. It was soon evident that only the loose surface oxide was being removed, and consequently the operation was continued using a motor-driven circular brush. After repeated

brushings the specimens still had coatings of black oxide which it was impossible to remove. The samples were weighed, however, in order to observe the agreement among several specimens.

Other wires were removed from the corrosion atmosphere and immersed in 15 per cent sulfuric acid containing 5 per cent of the inhibitor known as Barretts No. 20 pickling compound. The specimens soon became clean, and after being well washed with distilled water followed by alcohol and ether, they were dried with a soft cloth, allowed to stand in a desiccator for about an hour, and then weighed.

Other specimens were cleaned by heating them under a reflux condenser in a solution prepared by dissolving about 40 grams of citric acid in 100 cc. of ammonium hydroxide and adding excess ammonia. This treatment also left the metal bare in a short time.

Cournot and Chaussain (*1*) recommend treating the specimens with hot 20 per cent sodium hydroxide solution to which powdered zinc has been added. According to them, the violent evolution of hydrogen transforms the corroded layer into granules which fall to the bottom of the beaker. Several specimens were treated by this method.

The losses in weight of the specimens when the corrosion products have been removed by these different methods are given in Table I. Brushing is apparently worthless for these small specimens, the low weight losses indicating incomplete removal of the deposit, and the lack of agreement showing that not even qualitative results can be obtained. The samples cleaned by the other three methods showed fair agreement, not only among the samples cleaned by any one method, but also among the three different methods. The specimens cleaned by ammonium citrate were corroded in a different container from that used for the rest of the samples in order to see if the corroding process itself were reproducible. The results obtained were a little lower than those of the other three methods but are of the same order of magnitude and, from a practical standpoint, in fair agreement.

Table I. Loss of Weight of Specimens after Corrosion

Procedure	Loss on First Cleaning			Loss after 15 min. Additional	Difference from First Loss
	Gram	%	*Mg./sq. cm.*	*Mg./sq. cm.*	*Mg./sq. cm.*
Brushing	0.0236[a]	5.59	15.25	.....	....
Brushing	0.0128	3.17	8.27	.....	....
Brushing	0.0008	0.20	0.52	.....	....
Brushing	0.0020	0.48	1.29	.....	....
Brushing	0.0013	0.32	0.84	.....	....
Sulfuric acid and inhibitor	0.0481	11.52	31.07	31.46	0.39
Sulfuric acid and inhibitor	0.0560	12.98	36.18	36.43	0.25
Sulfuric acid and inhibitor	0.0494	11.86	31.91	32.49	0.58
Sulfuric acid and inhibitor	0.0354	8.68	22.87	22.87	none
Sulfuric acid and inhibitor	0.0366	8.91	23.64	23.84	0.20
Ammonium citrate	0.0343	8.73	22.08	22.48	0.40
Ammonium citrate	0.0290	7.16	18.73	18.73	none
Ammonium citrate	0.0303	8.03	19.57	19.64	0.07
Ammonium citrate	0.0291	7.20	18.91	19.19	0.28
Ammonium citrate	0.0338	8.79	21.83	21.83	none
Sodium hydroxide and zinc	0.0393	9.37	25.39	25.39	none
Sodium hydroxide and zinc	0.0492	11.70	31.78	31.78	none
Sodium hydroxide and zinc	0.0467	11.18	30.17	30.17	none
Sodium hydroxide and zinc	0.0445	11.30	28.75	28.75	none
Sodium hydroxide and zinc	0.0494	12.05	31.91	31.91	none

[a] Each specimen weighed approximately 0.40 gram, and had an area of approximately 1.50 sq. cm. Individual weights and areas were determined exactly.

The clean wires were then treated for 15 minutes more by the same method which had been used to remove the corrosion products, in order to learn the effect of the different procedures on the metal itself. The results are reported in Table I. Indications were that the sodium hydroxide and zinc treatment gave the best results, as no attack of the metal was found. It would appear that all three methods are about equally efficient in removing the deposit, but that acid and inhibitor and the ammonium citrate are liable to cause high results because of some attack of the clean metal. If the specimens are watched carefully as in these tests, however, the slight attack is not large enough to change materially the practical nature of the calculated results.

All traces of deposit appeared to have been removed by the treatments, but the possibility existed that the apparent attack of the metal might have been caused by the removal of some unnoticed scale left behind after the first pickling. In order to check this, some pieces of clean iron wire of the same stock and dimensions as the corrosion specimens were subjected to the different procedures. The wires were first pickled in sulfuric acid and inhibitor in order to remove any slight corrosion film that might have been on the surface. They were then washed with distilled water and finally immersed in alcohol and ether. After being wiped dry with a soft cloth, they were immediately placed in a desiccator and rapidly weighed. Five specimens were placed in each of the three cleaning solutions and left there for an hour. At the end of this period they were washed with water, alcohol, and ether, dried, and weighed. They were then replaced in the solutions for additional time and the total loss in weight found. Table II gives the average total loss in weight at the end of the indicated time periods of the five specimens treated by each method.

Table II. Effect of Procedures on Clean Metal

Procedure	Loss in Weight at End of: 60 min.	90 min.	180 min.
	Gram	*Gram*	*Gram*
Sulfuric acid and inhibitor	0.0012[a]	0.0013	.....
Ammonium citrate	0.0005	.....	0.0009
Sodium hydroxide and zinc	0.00006	0.00006	0.00008

[a] Each item is average of five specimens.

The sulfuric acid and inhibitor appear to attack the metal the most and the sodium hydroxide and zinc the least. The cause of the very low average for this last method is the fact that three specimens showed no weight loss at all. The sulfuric acid and inhibitor procedure is the easiest to use and would be advantageous if the attack of the metal did not affect the magnitude of the results. It is a little troublesome to use ammonium citrate, as it loses its effectiveness if the ammonia is driven off, necessitating the use of a reflux condenser.

Summary

The corrosion deposits can be removed from iron wire specimens by means of sulfuric acid and inhibitor, ammonium citrate, and sodium hydroxide and zinc, all three methods giving efficient removal of the deposit. The use of sodium hydroxide and zinc according to the procedure of Chaussain and Cournot is preferable, as it does not attack the bare iron.

Brushing as a means of removing deposit from small samples is worthless.

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Quantitative Determination of Formaldehyde and Benzaldehyde and Their Bisulfite Addition Products

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THE quantitative determination of aldehydes by their reaction with sodium bisulfite has long been known. The method consists of adding an excess of bisulfite to a solution of the aldehyde, allowing reaction 1 to take place, back-titrating the excess of bisulfite, and calculating the amount used by the aldehyde by difference.

$$RCHO + HSO_3^- = RCH(OH)SO_3^- \qquad (1)$$

The method is open to criticism, however, on account of the instability of bisulfite and, in the case of most aldehydes, the fact that the reaction is not complete. The direct determination of aldehyde bisulfite furnishes a simple and easy method for determination of the corresponding aldehyde. In the method developed here the reaction of the aldehyde and bisulfite is allowed to take place at the most favorable pH range, as determined by the work of Stewart and Donnally (*4*). After the reaction, the pH of the solution is changed to the range where the dissociation reaction

$$RCH(OH)SO_3^- = RCHO + HSO_3^- \qquad (2)$$

is slow, and the excess bisulfite is titrated with iodine solution (*5*).

Following this titration, the pH of the solution is again adjusted so that dissociation reaction 2 is fast, permitting titration of the aldehyde bisulfite compound with iodine solution. The rate of reaction of iodine and aldehyde bisulfite depends only upon reaction 2 and is independent of the concentration of iodine. The suitable pH ranges depend upon the particular aldehyde used.

Determination of Formaldehyde and Formaldehyde Bisulfite

Solutions Required

1. Standard iodine solution, 1 *M*
2. Sodium bisulfite solution, about 0.1 *M*
3. Sodium bicarbonate solution, about 1 *M*
4. Acetic acid solution, about 1 *M*
5. Sodium carbonate solution, about 1 *M*
6. Phosphoric acid solution, about 1 *M*

The dissociation constant of the sodium bisulfite solution for formaldehyde bisulfite is 1×10^{-7} at pH 6 (*1*), so that the reaction is sufficiently quantitative as long as the concentration of formaldehyde to be measured is not extremely low.

The following experiments illustrate the method used:

Five cubic centimeters of a sample of formaldehyde in water of approximately 0.4 *M* concentration were transferred by a pipet to a 250-cc. flask. Five cubic centimeters of 1 *M* sodium bicarbonate and 30 cc. of 0.1 *M* sodium bisulfite solution were then added (50 per cent excess bisulfite), and the solution mixture was allowed to stand a measured length of time. At the end of this time, 10 cc. of 1 *M* acetic acid and 2 cc. of starch solution were added. The excess bisulfite was then titrated and standard iodine solution was added to the first permanent end point. Next, 20 cc. of 1 *M* sodium carbonate were added, so the formaldehyde bisulfite compound could be titrated. In this titration it was desirable to keep the concentration of iodine as low as possible because of side reactions with formaldehyde, and the solution was therefore added, first 1 cc. at a time, then 0.5 cc., and finally drop by drop. The permanent end point with 1 drop of iodine in the solution lasted at least 10 minutes.

The results of these experiments are given in Table I, as well as results obtained by the method of difference. It will be seen that in 15 minutes the reaction goes to completion within two parts per thousand.

In order to check the method, the same solution was analyzed, using iodine and alkali according to a modified method of Romijn (*3*) and Fresenius (*2*). The modification consisted of increasing the alkali concentration to 1.6 *M* and allowing the reactants to stand for at least 20 minutes. The results obtained with this method are also given in Table I. The agreement between the two methods is well within two parts per thousand.

Table I. Results of Determination of Formaldehyde Solution

Minutes	Direct Titration with Iodine Iodine Cc.	Method of Difference Iodine Cc.	Oxidation of Formaldehyde Iodine Cc.
2	77.95	78.00	...
5	79.15	79.10	...
10	79.20	79.33	79.20
15	79.40	79.50	...
20	...	...	79.50
22	...	...	79.40
30	79.45	79.50	...

Determination of Benzaldehyde and Benzaldehyde Bisulfite

Reaction 1 in the case of benzaldehyde is not as complete as the corresponding reaction with formaldehyde. It is possible, however, to apply a correction to overcome this difficulty. The following analyses of benzaldehyde in water solution are presented as an example:

Thirty cubic centimeters of sample (approximately 0.04 *M*), 5 cc. of 1 *M* sodium bicarbonate, and 25 cc. of sodium bisulfite were put in a flask and allowed to stand a measured length of time. At the end of that time 10 cc. of 1 *M* phosphoric acid were added and the excess bisulfite not used by equation 1 was titrated as before with standard iodine solution. The end point here was a slowly fading one. Twenty-five cubic centimeters of 1 *M* sodium bicarbonate were then added and the solution further titrated with iodine to the permanent end point. This second titration represents the amount of benzaldehyde bisulfite.

Results of the series of measurements which were made by varying the time of contact of bisulfite and benzaldehyde are given in Table II, as well as results obtained with the method of difference. These results show that the method based upon difference is unreliable, giving a high result which is probably due to oxidation of bisulfite by oxygen.

Table II. Results of Determination of Benzaldehyde Solution

Minutes	Direct Titration with Iodine Iodine Cc.	Method of Difference Iodine Cc.	Bisulfite Discrepancy
2	23.40	23.50	0.1
5	23.35	23.95	0.6
10	23.45	24.05	0.6
24	23.40	24.80	1.4
30	23.50	25.20	1.7

These results give within one per cent the total amount of benzaldehyde in the solution, and if this accuracy is sufficient, nothing more need be done. However, a correction is easily applied in the following manner:

$$K = \frac{(PhCHO)\ (HSO_3^-)}{(PhCH(OH)SO_3^-)} \qquad (3)$$

and at pH 4 to 6, K equals 1.1×10^{-4}. The benzaldehyde bisulfite is 0.0195 M, and HSO_3^- is 0.0296 M. Solving for benzaldehyde in equation 3 we obtain 7.25×10^{-5} M or 4.35×10^{-6} moles of benzaldehyde, equivalent to 0.087 cc. of iodine. The correction to be applied is therefore 0.09 cc. of iodine.

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A Mechanical Device to Agitate Analytical Solutions by Swirling

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In the course of some experiments it was found necessary to agitate analytical solutions over a long period of time without the introduction of a stirrer. Since none of the conventional means of agitation met the necessary requirements, a device was developed whereby a swirling motion could be imparted to a solution analogous to that so common in the manual manipulation of analytical solutions. This device proved satisfactory for its intended use and has been otherwise serviceable in the laboratory.

The general appearance of the apparatus is shown in Figure 1. The base A carries a heavy vertical driving shaft, resting on a large ball bearing in the bottom socket. The plate C is bolted to the top end of the shaft and supports, by means of three ball bearings, the wooden platform B, the bottom of which is covered with a steel plate.

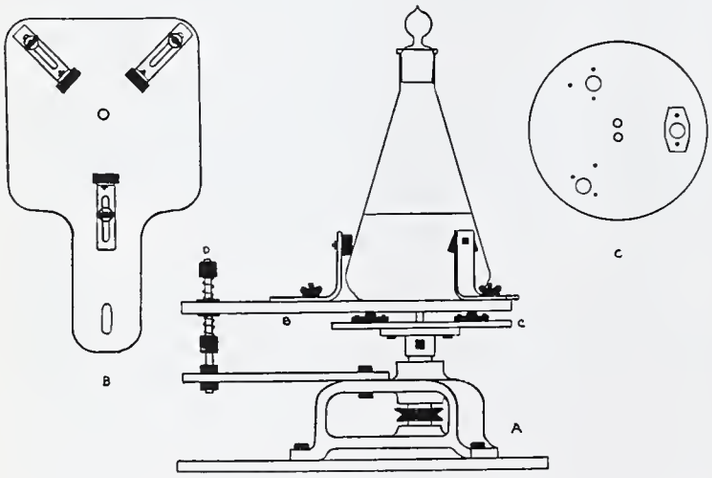

Figure 1

The driving element between the plate and the platform is a pin screwed to the plate slightly off-center and fitting into an opening in the center of the platform. Rotation of the platform is prevented by having the tail held in position by a pin, D, which passes through a small slot. The spring-washer arrangement, shown in the figure on D, serves to stabilize the platform. With this arrangement the rotation of the shaft gives to the head of the platform a circular motion, and a solution in a flask, clamped in position as shown, quickly picks up the desired swirling motion.

Most of the constructional details can be understood from the diagram, which is drawn to scale—the platform is 14.5 inches (36.8 cm.) long. A few additional observations, however, may be useful. The shaft is rotated at about 150 r. p. m. Two interchangeable positions for the pin are convenient, one 0.31 inch and the other 0.19 inch off-center. The three steel ball bearings are 0.625 inch and are held in position by suitable sockets bolted to the plate. In order to have a single race for the ball bearings, they must be equidistant from the pin for both positions of the pin. For this reason the plate is drilled and tapped so that the positions of the sockets can be changed. As a matter of fact, if the positions of the pins and sockets are taken as shown in the top view of the plate, it is only necessary to move one end of two sockets when the pin is changed from one hole to the other.

Although no systematic study of the question was made, it was observed that the degree of mixing attained is influenced to a large extent by the speed of rotation of the head of the platform. If the rotation is slow, the liquid in the vessel mounted on the platform gains only a simple, circular motion. However, when the speed of rotation is sufficiently great, the motion of the liquid becomes considerably more complex. On the surface there is at least one wave crest going around the wall of the flask, and internally, judging from the observed movements of particles of precipitate, there is a mode of motion best described as spiral. It is this last type of motion that produces most of the mixing. The efficiency of the mixing process varies somewhat with the bulk of the liquid, the shape of the container, and the eccentricity used. This last factor, it should be noted, is determined solely by the first two of the conditions just named. Although the efficiency of the mixing obtained by the present device is probably not equal in all cases to that obtained by manual manipulation, where the motion of the liquid is still more complicated, the method has the advantage that it can be continued over a long period of time without the attention of the operator. The apparatus described has been used successfully in agitating 300 cc. of solution contained in a beaker and also 2 liters of liquid in a 3-liter Erlenmeyer flask.

The apparatus described above was constructed from parts and material readily available in most laboratories. The mechanical details could, of course, be modified.

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Correction. In the article on "Shorter Method for Determining Copper Iodometrically" [Ind. Eng. Chem., Anal. Ed., 5, 15 (1933)] 10 cc. of 1.8 M potassium iodide solution should be added just prior to titrating with standard sodium thiosulfate solution. T. H. Whitehead

Colorimetric Determination of Thallium

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A colorimetric method for the quantitative determination of thallium in toxicological material, poison bait, or thallium salts, and utilizing the Hellige wedge type colorimeter, is described. The analysis of samples containing 10 to 75 mg. of thallium per kg. can be made on 10- to 20-gram samples and completed in 2 to 3 hours, within an accuracy of 3 to 5 per cent. The analysis may be shortened for thallium-coated grain and be completed in approximately 30 minutes. Details of procedure, preparation of standard, and calibration of wedge are given. The method has been found satisfactory in the presence of copper, lead, arsenic, mercury, molybdenum, and tungsten, but not in the presence of chromates. Illustrative results on tissues, urine, and thallium-coated grain are included.

THE increased usage of thallium in recent years, particularly as a rodenticide, has resulted in numerous instances requiring the determination of small amounts of thallium in toxicological material. The gravimetric and volumetric methods in general use are cumbersome and time consuming, require relatively large samples to obtain a weighable precipitate or appreciable titration, and in most instances are not highly accurate as applied to toxicological material. As an example, a study of the iodide method indicated that, by conducting the final washing of the precipitate with a saturated solution of thallous iodide, the results could be brought within an accuracy of ±0.2 mg. of thallium. On this basis, and desiring the analysis as a whole to be accurate within ±5 per cent, it would be necessary on material of approximately 25 mg. per kg. to use a sample weighing 160 grams, the oxidation and completion of the analysis requiring not less than 1 to 1.5 days.

The colorimetric method developed and here described requires 10- to 20-gram samples for material ranging from 10 to 75 mg. per kg. and is accurate to ±3 to 5 per cent, and the total time required is approximately 2 hours. On samples containing less than 10 mg. per kg., somewhat larger errors are to be expected.

OUTLINE OF METHOD

Organic matter is first destroyed by the Fresenius-v Babo process, following which thallic chloride is extracted from the filtrate with ether. Organic matter in the ether residue is destroyed with nitric and sulfuric acids, the nitrites resulting from this treatment being decomposed by evaporating the diluted acid solution to dryness after the addition of excess ammonium chloride. Thallous chloride contained in the residue is oxidized with a bromine solution, the excess being removed by boiling. Potassium iodide is added and iodine liberated as shown in the equation:

$$TlCl_3 + 2KI = TlCl + 2KCl + 2I$$

The liberated iodine is extracted with a measured volume of carbon disulfide, and the color intensity matched against a standard contained in the wedge of Hellige Universal colorimeter.

PREPARATION OF STANDARD AND CALIBRATION OF WEDGE

PROCEDURE. From a C. P. thallium salt, prepare a standard solution containing 0.2 gram of thallium per liter. Measure 16 cc. (3.2 mg.) into a 150–200 cc. narrow-necked flask and add 50 cc. of bromine solution, prepared by adding 100 cc. of concentrated hydrochloric acid and 100 grams of secondary sodium phosphate to 900 cc. of bromine water. Boil vigorously for 3 minutes while holding the flask with a clamp and rotating in a free flame. Cool, transfer to a 125-cc. separatory funnel, and adjust the volume to 60 cc. Add 5 cc. of potassium iodide solution (2 grams per liter), and 20 cc. of carbon disulfide. Stopper the funnel and shake for 15 to 30 seconds, allow the layers to separate, and fill the colorimeter wedge with the iodine standard obtained.

Calibrate the wedge by oxidizing 4-, 8-, and 12-cc. portions of thallium solution with 50 cc. of bromine, adding 5 cc. of potassium iodide and extracting with 20 cc. of carbon disulfide. Place these solutions as prepared in the colorimeter trough, match with the standard, and note the readings. On millimeter graph paper plot the readings against milligrams of thallium represented by each cubic centimeter of solvent. Further points should be determined if the graph does not form a straight line.

Figure 1 shows a typical graph, the reading for zero thallium content falling at 97, and each division below this point being equivalent to 0.00173 mg. of thallium per cc. of solvent:

$$\frac{0.168 \text{ (thallium content for zero reading)}}{97 \text{ (reading for zero thallium content)}} = 0.00173$$

Blank tests should be made on the bromine solution to determine the minimum time required for removing the excess, as continued boiling may produce low results. The hydrochloric acid tends to prevent reduction of thallic chloride in boiling solution and also increases the efficiency of the iodine extraction with carbon disulfide. Under the conditions specified, approximately 96 per cent of the theoretical amount of iodine is extracted, but the loss does not influence the accuracy of the method, since thallium determinations are made under the same conditions as the calibration. The purpose of the sodium phosphate in the oxidizing solution is to minimize the ionization of ferric salts in the samples analyzed and has no significance in the standardization other than to maintain similar extracting conditions. A volumetric method in which thallium is oxidized with bromine, and the influence of ferric ion eliminated by phosphate, has recently been published by Fridli (*2*). Owing to evaporation (even in a glass-stoppered wedge) and the action of light, the standard should be discarded and a fresh one prepared after 24 to 48 hours.

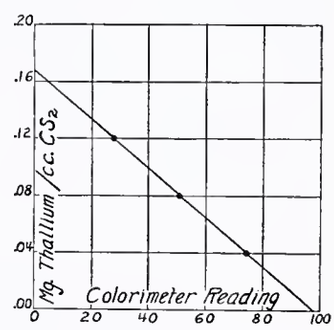

FIGURE 1. CALIBRATION CURVE

By proper adjustment between the weight of sample used and the volume of extracting solvent, the standard will apply to samples of any thallium content. For example, assuming a sample of approximately 2 mg. per kg. on which it is desired that the colorimeter will give a reading of approximately 10 divisions, we have:

$$\frac{0.00173 \times 1000 \times 10 \times \text{cc.}}{\text{weight of sample, grams}} = 2 \text{ mg. per kg.}$$

Solving for the required sample per cubic centimeter of solvent, we obtain 8.65 grams, or, for a 25-gram sample, we would use 3 cc. of extracting solvent.

As a second example, assume the sample to be coated grain of approximately one per cent; it is desired that the colorimeter will give a reading of say 50 divisions, and we have:

$$\frac{0.00173 \times 50 \times 100 \times \text{cc.}}{1000 \times \text{weight of sample}} = 1 \text{ per cent}$$

Solving for the required sample per cubic centimeter of solvent, we obtain 0.00865, or, for 20 cc. of solvent, we would use a sample weighing 0.173 gram.

The volume of bromine solution and potassium iodide should also be adjusted so that approximately constant conditions exist between the water phase and solvent.

Preliminary Treatment of Samples

Procedure. For toxicological material the weighed and finely divided sample is reduced to a fluid mass with 1 to 1 hydrochloric acid, brought to the boiling point on a water bath, and oxidized by successive additions of potassium chlorate in the usual manner. The cooled solution is filtered and washed to remove undecomposed fatty particles, and evaporated until a slight darkening is noted. Cool, transfer to a separatory funnel and add sufficient strong chlorine water to discharge the darkening and to leave considerable free chlorine in solution. Extract with two 50-cc. portions of ether for 1 to 2 minutes each, allow the layers to separate, and evaporate the ether portion in a narrow-necked flask. To the residue add 15 cc. of water, a few drops of hydrochloric acid, and 2 cc. of concentrated sulfuric acid. Insert a short-stemmed funnel in the neck of the flask, place on a hot plate, and evaporate to fumes of sulfur trioxide. Retain on the hot plate and at short intervals add fuming or concentrated nitric acid, a drop at a time through the funnel, until oxidation is complete and a colorless or light yellow solution remains. Cool, add 30 cc. of ammonium chloride solution (150 grams per liter), and evaporate to dryness while rotating in a free flame to prevent spattering. The analysis is completed by bromine oxidation, addition of potassium iodide, extraction, and color comparison as previously outlined. The entire procedure may be completed in 2 or 3 hours.

Thallium-coated grain does not require the chlorine oxidation or ether extraction unless treating a sample larger than 0.3 gram. The weighed sample is dissolved in fuming nitric acid containing 2 cc. of sulfuric acid, and evaporated to fumes of sulfur trioxide. Complete destruction of organic matter and the remainder of the analysis is carried out as above indicated. Determinations made in this manner can be completed in approximately 30 minutes.

Direct oxidation with nitric acid is satisfactory for urine samples sufficiently high in thallium to permit analysis on 5 cc. or less. If this is not the case, the complete determination should be used. Roughly, the direct method should not be used on urine containing less than 25 mg. of thallium per liter, or on grain containing less than 0.04 per cent of thallium.

Following the filtration from fat, some evaporation should occur, even though the volume is small, to promote a clean separation of the layers when extracting with ether. Excess chlorine is required during the extraction to maintain thallium in the thallic state, thallous salts being insoluble in ether. In the absence of free chlorine, thallium is reduced by the organic matter undecomposed by the preliminary treatment. Ether extraction of thallium was first suggested by Noyes, Bray, and Spear (*4*) for its qualitative detection, and has been found an effective method for its complete extraction; this procedure separates the thallium from many inorganic constituents and most of the undestroyed organic matter. Although ferric iron is also extracted by ether, no interference results from this element, owing to the later addition of phosphate which minimizes ionization of ferric salts.

The procedure outlined for complete destruction of organic matter in the ether residue was utilized by Baldeschwieler (*1*) in lead determinations on ethyl gasoline, and has proved very satisfactory. Other less drastic methods did not give as rapid or effective results. The reaction by this method is violent, but practically no mechanical loss occurs with a funnel inserted in the neck of the flask. A preliminary evaporation with water and a little hydrochloric acid tends to give a less violent reaction than occurs if sulfuric and nitric acids are added directly to the residue. A few drops of fuming nitric acid are usually sufficient to complete oxidation; however, if a large sample has been treated, more may be required, and additional sulfuric acid may be necessary to maintain a fluid condition.

The method employed for destruction of nitrites by evaporation to dryness in the presence of ammonium chloride was recently reported by Nelson, Levine, and Buchanan (*3*). Sufficient ammonium chloride should be present to react with all the free sulfuric acid, 15 cc. of 15 per cent solution being required for each cubic centimeter of sulfuric acid. While ammonium salts are present in the analysis and not in the standardization, they were found to have no appreciable effect on the extraction coefficient.

The hydrochloric acid, potassium iodide, and volume of the final solution should bear approximately the same ratio to the volume of carbon disulfide solvent as that maintained for the calibration of the wedge.

Summary of Experimental Data

Relation between Theoretical Iodine Liberated and Amount Extracted. The method outlined for preparation of the standard and calibration of the wedge resulted in a straight-line graph indicating consistent results for both large and small quantities of thallium when extraction conditions were held approximately constant. The method used does not determine, however, whether the actual amount of iodine extracted is identical with the theoretical quantity of iodine that should be liberated from the known quantity of thallium. To check this point, the wedge was filled with a standard containing a known quantity of iodine in carbon disulfide and calibrated with dilutions of the same solution with carbon disulfide. Aliquots of a standard thallium solution were also used to calibrate the iodine-filled wedge, and from these data it was determined that the iodine value obtained from thallium was 96 per cent of the theoretical value. To determine whether the low iodine value was due to incomplete oxidation and ionization of thallic iodide or to incomplete extraction, a standard aqueous solution of iodine was prepared, and aliquots of this were extracted with carbon disulfide after adjustment to the same volume and concentration of acid and potassium iodide. The extracted iodine when measured by the colorimeter was found to be 97 per cent of the value indicated by arsenious oxide standardization of the aqueous solution. Thus, within experimental limits of error, the low iodine value derived from thallium was shown to be due primarily to extraction loss.

Extraction Changes with Variation of Water Phase and Solvent. Experiments in which the carbon disulfide extractions were made in the presence of less hydrochloric acid and more potassium iodide gave results from 5 to 14 per cent below the actual values, these figures applying to one-tenth of the suggested acid content and to two to four times the usual amount of potassium iodide. At the usual acid content of 5 cc. per 60 cc. of water phase, additional amounts of potassium iodide caused only minor decreases in the percentage of iodine extracted.

Extractions made with the usual volume and composition of water phase, but with larger and smaller volumes of solvent, caused errors averaging −1.3 per cent with 5 cc. of solvent, and averaging +2.3 per cent with 40 cc. of solvent. As these errors are not large, it is evident that the ratio between volume of water and solvent need be adjusted only roughly to insure consistent results. As 5 cc. of potassium iodide are sufficient to react with approximately 6 mg. of thallium, it is evident (assuming constant ratios are maintained) that the

limiting factor is the upper limit of the standard rather than the amount of potassium iodide present.

Analysis of c. p. Thallium Salts. The method developed is essentially for samples of low thallium content, but is satisfactory and extremely rapid for the assay of high percentage salts where an accuracy greater than ±2 per cent is not required. Analysis of the c. p. acetate, chloride, nitrate, and carbonate gave values varying from the theoretical thallium percentage by 0.13 to 1.76 per cent. At the other extreme, analyses of small samples containing 0.04 to 0.1 mg. gave values in error by 3 to 5 per cent.

Interference by Other Metals. Analyses were conducted on aliquots containing 0.5 mg. of thallium to which were added 5 mg. of another metal in the form of a soluble salt. These tests were made on copper, lead, iron, arsenic, mercury, tungsten, and molybdenum, the complete analysis being used exclusive of the preliminary oxidation with potassium chlorate. The values obtained were in all cases within 0.01 to 0.02 mg. of the true value, indicating no appreciable interference by the metals tested. Attempts to assay thallium chromate by the colorimetric method were not successful, however. No method was found to eliminate satisfactorily the chromate interference.

Prepared Samples and Blanks. A number of blank tests were made on 20-gram samples of beef heart and liver, the iodine values obtained ranging from 0.01 to 0.02 mg. of thallium. Prepared samples containing 0.5 mg. of thallium per 20 grams of meat were carried through the complete analysis with errors of 1 to 5 per cent.

Illustrative Results on Grain, Urine, and Tissues. Thallium-coated wheat, prepared on the ratio of one pound of thallium sulfate to 100 pounds of wheat, and thus containing 0.81 per cent of metallic thallium, was used for analysis. Five analyses on individual kernels made by direct nitric acid oxidation gave values from 0.605 to 1.11 per cent, the average being 0.834. These results indicate the variation that may be expected from the analysis of single kernels owing to unequal distribution of the thallium. A 3-gram sample of the same material (approximately seventy-five kernels) was pulverized and thoroughly mixed. Two analyses from this sample gave values of 0.79 and 0.84 per cent, the average being 0.815. Three blank tests run on strychnine-coated barley did not liberate a measurable quantity of iodine in any case.

A dog was given thallium sulfate by capsule, equivalent to 25 mg. of thallium per kg. of body weight. The animal was placed in a metabolism cage, and the total urine for each day collected. Triple analyses on the samples for the first two days show the checks obtained: first day, 24.4 ± 0.4 mg.; second day, 13.9 ± 0.3 mg. Blank tests made on normal urine gave zero values.

The following data are illustrative of results obtained on tissues from thallium-poisoned game birds on which a complete report will appear elsewhere. The values shown are on heart muscle from thallium-poisoned geese:

Thallium Dosage	Time until Death	Thallium Found	Thallium Dosage	Time until Death	Thallium Found
Mg./kg.	*Days*	*Mg./kg.*	*Mg./kg.*	*Days*	*Mg./kg.*
40	1	33.2	32	8	20.0
28	2	25.3	20	13	10.1

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(3) Nelson, G. H., Levine, Max, and Buchanan, J. H., Ind. Eng. Chem., Anal. Ed., 4, 56 (1932).
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Microdetermination of Calcium in Sea Water

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For many investigations in oceanography and marine biology information concerning the calcium content of sea water is required. Previous workers have determined calcium in sea water by precipitating with oxalate, igniting, and weighing as the oxide. A summary of the results obtained is given by Thompson and Wright (*4*), who also determined the concentration of calcium in water from the Puget Sound and the Gulf of Alaska. They found that in these regions calcium bears a constant ratio to the chloride, and computations made from the data of other investigators indicated that this is the case also in other parts of the sea. It is especially noteworthy that 77 samples collected by the *Challenger* Expedition from various parts of the world and analyzed by Dittmar (*1*) gave an average calcium-chloride ratio but slightly higher than that obtained by Thompson and Wright.

It thus appears that for most purposes the calcium content of normal sea water can be calculated with sufficient accuracy from the chlorinity or from some other easily determined component or property of the water directly related to the chlorinity. However, there is often need for determining calcium in connection with experimental studies in which sea water is used and in investigating water from localities where calcium salts may be dissolved or precipitated. For many such investigations, which usually call for numerous analyses, the standard gravimetric method is too time-consuming and requires larger samples than are often available. For that reason the applicability to sea-water analysis of the microcalcium method described by Kirk and Schmidt (*2*) was studied and it was found to give satisfactory results after certain modifications were made. Because of these modifications and because of the necessity for close attention to certain details, a rather detailed description of the technic finally adopted is given in this paper.

Nearly all the chemical constituents of sea water vary with depth and this is true also of a number of factors which affect the solubility of calcium salts. By several workers calcium has been determined in water from various depths of the sea, but there is no record of a detailed study of its vertical distribution in any locality. After perfecting the analytical method, such a study was consequently made and the results, which also indicate the order of accuracy of the method, are included in this paper.

Method

Apparatus and Reagents. The apparatus needed for the determination of calcium in sea water is the same as that used by Kirk and Schmidt (*2*). It consists primarily of a set of microfilters (obtainable from the Central Scientific Co., Chicago, Ill.) which have been described in detail in the above-mentioned article. These are inserted in rubber stoppers which have been cut to half their usual thickness and placed in a battery of suction flasks attached to a vacuum manifold. In addition, beakers of 150 ml. capacity, with watch glasses and small stirring rods to fit, are required.

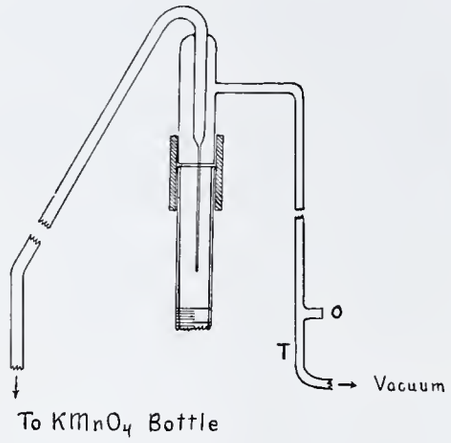

Figure 1

Two special wash bottles are desirable, one for ammonia and one for 2 *N* sulfuric acid. The ammonia bottle should be fitted with a plain rubber bulb having no intake valve, thus making it easy to stop the flow of ammonia by simply releasing the pressure on the bulb. The acid wash bottle is conveniently made from an Erlenmeyer flask of about 200 ml. capacity and should have an outlet tube with a fairly fine tip and an air intake extending to the bottom of the bottle. This bottle is used by inverting it, thus allowing the acid to flow out in a fine stream, and it should be wrapped with asbestos or some other material which is a relatively poor conductor of heat, since the acid is heated before use. For the titrations, a 10-ml. buret calibrated in 0.02 ml. is desirable. In order to avoid contact of permanganate with rubber, and to simplify the filling of the buret, a convenient attachment is shown in Figure 1. Its use is practically self-explanatory. If a vacuum line is available, the tube *T* is attached to it, the vacuum cock opened slightly, and the outlet *O* is closed with the fingers to fill the buret. Simply removing the finger stops the flow.

The reagents needed are as follows:

1. Potassium permanganate solution, approximately 0.06 *N*, kept in a dark bottle. This solution is made by dissolving about 2.0 grams of potassium permanganate in each liter of solution and allowing to stand at least 24 hours in a clean glass-stoppered bottle to permit the manganic oxide to settle out. The solution is then filtered through sintered glass into the stock bottle, or if such filters are not available, it may be carefully siphoned into the bottle, being careful not to disturb the layer of manganic oxide, and discarding the first solution coming through the siphon and the last inch in the bottom of the original bottle. The permanganate must never come in contact with rubber or other organic matter. It is standardized against pure sodium oxalate or oxalic acid. The sodium oxalate obtainable from the Bureau of Standards is to be preferred. Permanganate approximately 0.06 *N* is chosen because about 9 ml. of this solution will titrate the calcium from 25 ml. of sea water.
2. Ammonium oxalate solution, 4 per cent.
3. Hydrochloric acid solution made by diluting 1 volume of concentrated acid with 3 volumes of water.
4. Ammonium hydroxide solution, approximately 2 *N*.
5. Sulfuric acid solution, approximately 2 *N*.
6. Ammonium hydroxide solution, about 1 to 6, saturated with calcium oxalate. This is filtered before use.
7. Bromocresol purple solution, 0.5 per cent.
8. Asbestos, preferably short fiber, Italian, washed and ignited (obtainable from the J. T. Baker Chemical Co., Phillipsburg, N. J.). Before use this is rubbed in a mortar to shorten the fibers further, after which it is heated with dilute sulfuric acid. Potassium permanganate is added to a faint permanent pink, followed by more heating. When it no longer discolors permanganate it is thoroughly washed with water and finally suspended in a flask of water. Such asbestos gives no blank titration with permanganate.

Procedure. A sample of sea water is measured with a 25-ml. pipet into a 150-ml. beaker. About 10 ml. of hydrochloric acid solution are added, followed by 20 ml. of ammonium oxalate solution. One drop of bromocresol purple is added and the solution heated on an electric hot plate. When the solution begins to steam, 2 *N* ammonium hydroxide is added slowly with stirring to the turning point of the indicator. The last portions should be added drop by drop. The hot solution is removed from the hot plate and covered with a watch glass. The solution, which should be faintly purple when cool, is allowed to stand about 4 hours and is then filtered through the microfilters mentioned above.

A filter is prepared by first placing the platinum disk on the shoulder of the glass portion, making sure it is squarely seated. Asbestos, treated as described above, is next run in, preferably from a pipet with an enlarged orifice. Enough is used to form a layer about 1 mm. thick. This is washed under vacuum two or three times. In case the filter so formed filters unusually slowly, it is advisable to add a few milliliters of alcohol, followed by a little ether. Water is again used following the ether. This treatment will increase the speed of filtration in nearly every case.

The outside of the lip of the beaker containing the solution is greased with a little vaseline to prevent loss of precipitate over the edge, after which the solution is filtered under a mild vacuum. The inside of the beaker is rinsed with one portion of dilute ammonia saturated with calcium oxalate. (This solution should contain no excess oxalate and is conveniently used in the ammonia wash bottle described above.) This wash solution is passed through the filter.

The filter pad and disk are now pushed out of the filter into the beaker by means of the stirring rod which should be small enough in diameter to be inserted easily through the bottom of the filter. The calcium oxalate which adheres to the sides of the filter is washed out first with a little water, then with hot 2 *N* sulfuric acid from the acid wash bottle, and finally with a little more water. The sides of the beaker are washed down with the hot acid and the solution is ready for its second precipitation. This is carried out exactly as before by adding 20 ml. of ammonium oxalate, one drop of bromocresol purple and then ammonia to the hot solution to the turning point of the indicator. The hydrochloric acid is omitted, since the solution is already strongly acid. The solution is allowed to stand 4 hours and is filtered again exactly as before. This brings the total asbestos in the filter to twice the usual amount, but does not change the speed of filtration appreciably. The washing of the second precipitate must be carried out carefully. The authors habitually use three rinsings of the beaker and two further washings of the filter with the dilute ammonia saturated with calcium oxalate. The precipitate, filter pad, and disk are transferred to the precipitation beaker as before with hot sulfuric acid and are then ready to be titrated with the permanganate solution.

For the titration, the precautions are the usual ones for permanganate titrations. The solution should be at about

70° C., especially at the end point, and the permanganate is not added faster than it can be decolorized. The first permanent pink is the end point.

Discussion of Method

Sea water contains approximately three times as much magnesium as calcium. With so large an excess of magnesium it has so far proved impossible to adjust the conditions so as completely to separate the two elements in one precipitation. The amount of magnesium oxalate occluded on the calcium oxalate after the first precipitation represents about 6 to 8 per cent of the total oxalate precipitated. Thompson and Wright (*4*) used triplicate precipitations and present data to show that this is essential. They do not state their method of precipitation, but presumably they followed the usual procedure of making the solution definitely alkaline with ammonia. If so, the necessity for three precipitations can readily be explained, since in alkaline solution much larger quantities of magnesium oxalate are occluded than in neutral or slightly acid solutions. The authors have repeatedly used two and three precipitations on identical samples of sea water and find identical values for the titration within the limit of accuracy of the method.

The presence of ammonium chloride has long been thought to aid in preventing the occlusion of magnesium oxalate. The authors have not specifically checked this point, though in a recent publication Popoff, Waldbauer, and McCann (*3*) state that ammonium chloride has no influence, and also point out that long digestion in alkaline solution increases the magnesium content of the precipitate. The present authors have not used an alkaline solution nor long digestion, inasmuch as at the pH chosen the size of crystals is very satisfactory and long digestion is entirely unnecessary. Like the above-mentioned investigators, they have found that the amount of ammonium oxalate added is the most important factor. They have used 5, 10, and 20 ml. of ammonium oxalate, and get consistent results and complete recovery only when 20 ml. are used.

Experimental

In order to determine the absolute accuracy of which this method is capable, the authors prepared from reagent chemicals a solution to contain calcium, magnesium, and sodium, in practically the same concentrations as in sea water. (Some difficulty was experienced in obtaining calcium-free magnesium sulfate.) Of this solution five identical samples were analyzed. The results, which are shown in Table I, indicate a maximum error of ±0.7 per cent.

Table I. Analysis of a Solution of Known Calcium Content

Calcium Present	Calcium Found	Difference	
Mg.	*Mg.*	*Mg.*	%
5.64	5.66	+0.02	+0.35
5.64	5.60	−0.04	−0.71
5.64	5.68	+0.04	+0.71
5.64	5.66	+0.02	+0.35
5.64	5.63	−0.01	−0.18
Average	5.646	±0.026	±0.46
Maximum		±0.04	±0.71

The method was further checked by analyzing a set of sea-water samples to half of which had been added known and varying quantities of calcium. Table II shows the results. It may be noted that six analyses of the original water gave an average calcium content of 10.40 mg. per sample with a maximum range of 0.07 mg. The samples to which calcium had been added gave practically the same average after correcting for the added calcium.

Table II. Analysis of Sea Water Containing Varying Quantities of Calcium

(All calcium values for 25-ml. samples)

Original Calcium	Calcium Added	Total Calcium Found	Calcium Found Minus Calcium Added
Mg.	*Mg.*	*Mg.*	*Mg.*
10.06	1.13	11.16	10.03
10.04	2.26	12.32	10.06
10.02	2.26	12.30	10.04
10.03	2.26	12.24	9.98
10.02	2.26	12.31	10.05
10.09	5.64	15.61	9.97[a]
	5.64	15.60	9.96[a]
Average 10.043			10.032

[a] Values omitted in computing average because upper limit of recoverable quantity of calcium is apparently reached at about this point.

To ascertain the variation in the calcium content with depth along the coast of southern California and to obtain data for comparing with results obtained by other methods and for other localities, calcium was determined on seventeen water samples collected on July 14, 1931, from different depths at a point ten miles seaward from the Scripps Institution pier. The samples were also analyzed for chloride and the results are shown in Table III. This table gives further information regarding the relative accuracy of the calcium method, the maximum deviation from the average of two determinations being 2.4 mg. per kg., corresponding to about ±0.5 per cent. For all but five of the seventeen samples the deviation is less than 1.0 mg. per kg.

Table III. Calcium in Sea Water from Various Depths

		Calcium				Ratio Ca:Cl		
Depth	Cl	A	B	Av.	Deviation from av.	A	B	Av.
Meters	*G./kg.*	*G./kg.*	*G./kg.*	*G./kg.*	*G./kg.*			
0	18.78	0.4055	0.4048	0.4052	0.0004	0.02159	0.02155	0.02157
5	18.78	0.4040	0.4063	0.4052	0.0012	0.02151	0.02163	0.02157
10	18.77	0.4063	0.4075	0.4069	0.0006	0.02165	0.02171	0.02168
15	18.72	0.4056	0.4064	0.4060	0.0004	0.02167	0.02171	0.02169
20	18.70	0.4056	0.4067	0.4062	0.0006	0.02169	0.02175	0.02172
25	18.67	0.3974	0.4017	0.3996	0.0022	0.02129	0.02152	0.02141
30	18.62	0.4014	0.4017	0.4016	0.0002	0.02156	0.02157	0.02157
35	18.60	0.3986	0.3982	0.3984	0.0002	0.02143	0.02141	0.02142
40	18.61	0.4010	0.4010	0.4010	0.	0.02155	0.02155	0.02155
50	18.61	0.4014	0.4017	0.4016	0.0002	0.02157	0.02159	0.02158
75	18.70	0.4048	0.4056	0.4052	0.0004	0.02165	0.02169	0.02167
100	18.78	0.4001	0.4028	0.4015	0.0014	0.02130	0.02145	0.02138
150	18.86	0.4071	0.4024	0.4048	0.0024	0.02159	0.02134	0.02147
200	18.96	0.4051	0.4062	0.4057	0.0006	0.02137	0.02142	0.02140
250	19.04	0.4116	0.4089	0.4103	0.0014	0.02162	0.02148	0.02155
300	19.01	0.4062	0.4081	0.4072	0.0010	0.02137	0.02147	0.02142
400	19.00	0.4089	0.4105	0.4097	0.0008	0.02152	0.02161	0.02157
Av.	18.77	....	....	0.4045	0.0008	.....	.....	0.02154
Max.	19.04	....	....	0.4103	0.0024	.....	.....	0.02172
Min.	18.60	....	....	0.3984	0.	.....	.....	0.02138
Diff.	0.44	....	....	0.0119	0.0024	.....	.....	0.00034

The average calcium content of the water was found to be 0.405 gram per kg. A slight variation with depth is indicated, corresponding in general with the variation in chlorinity which is clearly shown in the table. The average calcium-chloride ratio is 0.02154, which is in remarkably close agreement with the ratio, 0.02150, found by the careful work of Thompson and Wright (*4*). It is to be noted that these authors analyzed water mainly from the Puget Sound and the Gulf of Georgia, where the chlorinity is decidedly lower than along the California coast. Their ratios, which represent composite samples, are somewhat more constant than those in the present investigation, ranging from 0.02139 to 0.02160, as compared with a range from 0.02138 to 0.02172.

From their results Thompson and Wright conclude that in sea water calcium occurs in constant ratio to the chlorinity, within the limits of accuracy of the analytical methods. In general, the same is true of the region investigated here, but in the case of some of the samples the variation in the ratios is not wholly attributable to known experimental errors, and the results at least suggest that in certain parts

of the sea biological activity or other factors may affect the calcium content of the water to a measurable extent. Further investigation of this subject is desirable and may throw some light on certain geological and biological phenomena taking place in the sea.

Summary

A micromethod for determining calcium has been adapted to the analysis of sea water and the technic is described in detail. The method is comparatively rapid and is capable of an accuracy of about 0.5 per cent or better.

The results of calcium determinations on sea water from various depths are reported. These results confirm the conclusion drawn by previous workers that in sea water calcium is one of the substances present in constant proportion of the total salt.

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Relation between Volume of Respiration Chamber and Concentration of Carbon Dioxide in End Sample and in Composite Sample of Air

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For the measurement of the production of carbon dioxide and the consumption of oxygen, the subject of the experiment is either connected to or enclosed in a respiration apparatus. The first method implies the use of a mouthpiece with nose clamp, as generally used on humans for purposes of clinical research; or connection by means of a tracheotomy tube in the case of animals. For those experiments with animals in which tracheotomy is to be avoided, the second method must be used. The animal is enclosed in a respiration chamber which is generally connected to a ventilating system.

For the construction of a respiration apparatus for measuring the metabolism of animals, it is of interest to know the relation between the volume of the chamber, the rate of ventilation, the rate of respiratory exchange, and the concentration of the carbon dioxide and oxygen in the chamber. The degree of accuracy of the result of a trial may then be predicted, provided this degree is limited by the accuracy of the gas analysis.

With a given rate of production in a chamber and at a certain rate of ventilation, the concentration of the product (for example, carbon dioxide) is the smaller, the larger the chamber. The knowledge of this general relation is, however, inadequate for estimating the influence of a certain error in gas analysis upon the error in the result of an experiment. For that purpose the functions must be expressed in mathematical terms. The equations for these relations seem not to have been worked out. For a part of the problem (concentration of carbon dioxide in a sample taken at a certain moment) the author developed the equation in an earlier study (*1*). The present paper shows that in many cases the composition of the composite sample is more important than that of the momentary samples, and carries out the calculation for the influence of the volume of the chamber, the rate of ventilation, and the rate of production upon the composition of the composite sample. An equation is given from which investigators in this field can predict the influence of an error in gas analysis upon the error in the result for any apparatus. This is a guide for the selection of the apparatus for a given purpose.

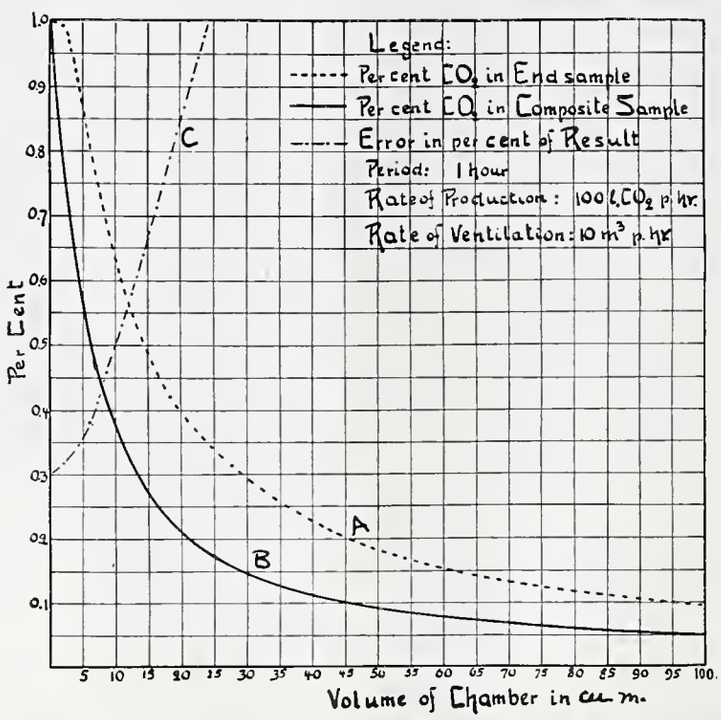

Figure 1. Influence of Volume of Chamber on Concentration of Carbon Dioxide and Resulting Error

Relative Significance of Momentary and Composite Samples

In an apparatus of the Tigerstedt type, a momentary sample is taken from the air in the chamber at the beginning and at the end of a period, and a composite sample which consists of small amounts of the air taken regularly during the experiment is collected. The result for the carbon dioxide production is calculated according to the equation:

$$R = V(C_e - C_0) + L \times t \times C_m$$

where

R = amount of carbon dioxide produced in the chamber in liters
V = volume of chamber in liters
L = intensity of ventilation (liters per hour)
t = time in hours
C_0 = concentration of carbon dioxide at the start (momentary sample)

C_e = concentration of carbon dioxide at the end (momentary sample)
C_m = concentration of carbon dioxide in the composite sample

The analysis of the composite sample becomes the more important the larger the amount of air sucked through (compared with the volume of the chamber). The ratio $\frac{Lt}{V}$ may be called the relative significance of C_m and $(C_e - C_0)$—i. e., the ratio of the amounts which are contributed to the result per unit of C_m and $(C_e - C_0)$, respectively. Thus, with a chamber of 10 cubic meters capacity and a rate of ventilation of 10 cubic meters per hour, the relative significance of C_m and $(C_e - C_0)$ would be expressed by the duration of the period in hours. For a period of 1 hour, C_m would have the same significance for the result as $(C_e - C_0)$. If f_i be the error of the difference $(C_e - C_0)$, and f_c the error of C_m, the error of the result due to these errors in gas analysis would be $\sqrt{f_i^2 + f_c^2}$.

If, under the same conditions, a period of 10 hours is considered, the significance of the analysis of the composite sample (C_m) would be 10 times the significance of the difference between the analyses of the start and end samples $(C_e - C_0)$. The error due to the error in gas analysis would become $\sqrt{f_i^2 + (10f_c)^2}$. If f_i and f_c are of the same magnitude,[1] it follows that for the 10-hour period, the error of $(C_e - C_0)$ contributes only 1 per cent of the error of C_m. On account of the dominating role of the composite sample for the result of experiments of long duration, the author has continued his earlier studies on the relation between the volume of the chamber and the concentration of the carbon dioxide in the momentary samples, and has also calculated the influence of the volume of the chamber on the concentration of the composite sample (C_m).

Influence of the Volume of the Chamber upon Composition of Composite Sample

The following equation was developed in the paper mentioned above (*1*):

$$C_e = C_0 \times e^{-\frac{L}{V}t} + \left(\frac{\gamma}{L} + c_i\right)\left(1 - e^{-\frac{L}{V}t}\right) \qquad (1)$$

where

C_e = concentration of carbon dioxide in air in chamber at end of period (liters of carbon dioxide per liter of air)
C_0 = concentration of carbon dioxide in air in chamber at start of period
c_i = concentration of carbon dioxide in air flowing from outside into chamber
L = intensity of ventilation (liters of air sucked out from chamber per hour)
V = volume of chamber in liters
t = duration of period in hours
γ = intensity of carbon dioxide production in chamber (liters of carbon dioxide per hour)

In order to study the influence of the volume of the chamber on the accuracy of the result, the calculation may be simplified. The concentration of the carbon dioxide at the start of the period and also the concentration in the inflowing air may be taken as zero. Thus, what is calculated is not the actual end concentration, but only that part of it which is due to the carbon dioxide production inside the chamber.

The result of this simplification is

$$C_{e(p)} = \frac{\gamma}{L}\left(1 - e^{-\frac{L}{V}t}\right) \qquad (1')$$

[1] If the error in gas analysis is the same, the error of the difference of the two analyses (f_i) is in fact not equal to the error of the composite sample (f_c), but f_i is $f_c \times \sqrt{2}$. The factor, $\sqrt{2}$, does not alter our conclusions and therefore has been omitted for simplicity.

It follows from this equation that for a very small chamber $(V \longrightarrow 0)$, $C_{e(p)}$ becomes $\frac{\gamma}{L}$. This is the case for the methods in which the animal is connected to, instead of enclosed in, the respiration apparatus. The result of this equation for a certain rate of production (c = 100 liters per hour) and a certain rate of ventilation ($L = 10 \times 10^3$ liters per hour) is shown as curve *A*, Figure 1.

In order to calculate the influence of the volume of the chamber on the concentration of the carbon dioxide in the composite sample, the following procedure may be chosen:

If v be the volume of the composite sample at the time t, the amount of carbon dioxide in this sample will be $C_m \times v$. This amount is the summation of the small amounts dv taken at regular intervals (which could be chosen indefinitely small). The amount of carbon dioxide brought to the sampler at the end of the short period 1 will be $C_{e(1)} \times dv$; the amount added during the period i will be $C_{e(i)} \times dv$ ..... etc., where C_e is used as in equation 1, meaning the concentration of the carbon dioxide in the chamber at a certain moment. The total amount of carbon dioxide in the composite sample, which is the product of the mean concentration C_m and the volume, is the sum of all added amounts.

Thus

$$C_m \times v = C_{e(1)} \times dv + C_{e(2)} \times dv + \ldots + C_{e(i)} \times dv + \ldots$$

or

$$C_m = \frac{1}{v}\int_0^v C_e \times dv \qquad (2)$$

If s be the intensity of the air flow to the collector of the sample (presumed to be constant), the small increase of the sample dv is equal to $s \times dt$ and the end volume of the sample is $v = s \times t$. If the values for v in equation 2 are thus substituted, s is canceled out and it follows that

$$C_m = \frac{1}{t}\int_{t=0}^{t=t} C_e \times dt \qquad (3)$$

Using the result for C_e from equation 1, the following equation is obtained:

$$C_m = \frac{1}{t}\int_{t=0}^{t=t}\left[C_0 \times e^{-\frac{L}{V}t} + \frac{\gamma}{L} + c_i - \left(\frac{\gamma}{L} + c_i\right)e^{-\frac{L}{V}t}\right]dt \qquad (4)$$

the integration of which leads to the following result:

$$C_m = \frac{\gamma}{L} + c_i - \frac{V}{L \times t}\left[C_0 - \left(\frac{\gamma}{L} + c_i\right)\right]\left(e^{-\frac{L}{V}t} - 1\right) \qquad (5)$$

With the simplifications made above—namely $c_i = 0$ and $C_0 = 0$—this equation is reduced to

$$C_{m(p)} = \frac{\gamma}{L}\left[1 - \frac{V}{Lt}\left(1 - e^{-\frac{L}{V}t}\right)\right] \qquad (5')$$

The result of this equation for a period of 1 hour, a rate of production of 100 liters of carbon dioxide per hour, and a rate of ventilation of 10 cubic meters per hour as an example is shown on Figure 1, Curve *B*.

The error of the result due to the errors in gas analysis is increased with the increase of the volume of the chamber.

If the error in analysis of the composite sample is equal to 0.003 per cent of the air volume, and the error in analysis of the difference between the initial concentration and end con-

centration in the air of the chamber is equal to 0.004 per cent, then the error of the result will be

$$\pm\sqrt{(0.003 \times 10^{-2} \times Lt)^2 + (0.004 \times 10^{-2} \times V)^2}$$

or in the case shown on the figure ($t = 1$, $L = 10 \times 10^3$)

$$\pm\sqrt{0.09 + (0.004 \times 10^{-2} \times V)^2}$$

Curve C on Figure 1 shows the increase of the error as the volume of the chamber increases according to the assumptions made.

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Preparation of Aldehyde-Free Ethyl Alcohol

Rapid Method

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Current methods for the preparation of water-white alcoholic potassium or sodium hydroxide solutions are far from satisfactory, being not only uneconomical of time and materials but inconstant of performance in so far as they do not lead with certainty to the desired end. There is, therefore, an obvious need for an inexpensive method which will efficiently and rapidly remove the troublesome aldehydes, to which, in virtue of their forming brown resinous products with alkalies, the discoloration of the so-called alcoholic potash (or soda) solution is primarily ascribed.

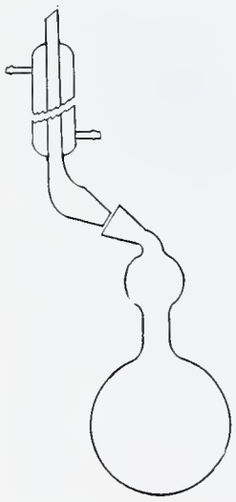

Figure 1. Combination Reflux and Distillation Apparatus

The methods for accomplishing these ends are of two kinds, preventive and remedial. In the former group there are several which merit mention. First, there is the time-honored procedure, to which both the Association of Official Agricultural Chemists and the American Society for Testing Materials have given approval, of letting the raw alcohol stand in contact with potassium hydroxide for several days or of hastening the reaction by digesting the mixture for hours under reflux. Doubtless many an analyst following this procedure has been annoyed by the discovery that his labors have yielded a product of unsatisfactory character, a distillate which was obtained at some sacrifice of expensive solvent, because of incomplete recovery of the solvent from the alkaline reaction mixture.

Then there is the procedure of Dunlap (*4*), who appears to have based his method upon a suggestion of Winkler (*6*) that the use of silver oxide under prescribed conditions leads to the preparation of an anhydrous product. The analyst, however, must anticipate his needs well in advance of use and must be satisfied with a product whose water content has been slightly increased, inasmuch as the silver oxide is formed *in situ* from reagents, one of which is in aqueous solution. This method for making ethyl alcohol aldehyde-free, or substantially so, is not necessarily expensive, because the silver can be recovered and little alcohol is lost during purification. This procedure has received recognition in the U. S. Pharmacopeia.

Finally, there is the method which is used in the purification of ethyl alcohol for determination of aldehydes in citrus flavoring extracts (*2*). Chace (*3*) seems to be responsible for this mode of procedure, which embodies the use of *m*-phenylenediamine hydrochloride. A 48-hour digestion period of this reagent with the alcohol must precede distillation, the permissible recovery being approximately 85 per cent.

In the second group, or remedial methods, is one which to date seems to have passed unnoticed. It is suggested by Englis and Mills (*5*), who found that the addition of sodium hydrosulfite to a discolored alcoholic potash solution is effective, although the reaction rate is exceedingly slow. This method is, however, essentially a preventive one, in that the recommended course of procedure is to add the hydrosulfite to the alcoholic alkali solution immediately after it has been prepared. The reaction whereby discoloration is prevented is probably twofold: the inhibition of the photochemical decomposition of alcohol to aldehyde, and the reduction of any aldehyde present *per se* to alcohol. Fundamentally, however, the analyst does not get away from the necessity of beginning his preparation with a solvent which is substantially free of aldehydes.

The method herein proposed, in part suggested by the observations of Englis and Mills, rests upon an application of the fact that nascent hydrogen reduces an aldehyde to its corresponding alcohol at moderate temperatures. This reaction, which is an exothermic one, is brought about by adding to the raw alcohol potassium hydroxide and metallic aluminum, or any metal or alloy yielding hydrogen under these conditions, and digesting the whole for a short time. Zinc may be substituted for the aluminum, but because it is slower to react with alkali than aluminum, its use in the treatment of a product relatively high in aldehyde content will require a longer digestion period. Sodium amalgam may also be used to effect the reduction, but recourse to this reagent hardly seems necessary unless one desires to prepare a product which is both water- and aldehyde-free.

Since the alcohol of commerce is relatively low in aldehyde content, a satisfactory degree of reduction will be obtained without a preliminary digestion by the addition of 5 to 10 grams of the metal in granular form and 8 to 10 grams of potassium hydroxide to one liter of alcohol. Ethyl alcohol containing 0.2 per cent added acetaldehyde has been successfully treated by this method by refluxing the reaction mixture for one hour before distillation.

The efficiency of the proposed procedure for removing aldehyde from ethyl alcohol was demonstrated by the following experiment, in which conditions far more drastic than any likely to be met with in actual work were set up. Separate portions of a standard solution of acetaldehyde (17 mg. per cc.) in purified alcohol were treated, respectively, with potassium hydroxide and aluminum, and with alkali only. Both solutions were then subjected to reflux distillation, during the course of which samples were withdrawn from time to time for analysis as to aldehyde content (*1*).

Table I. Comparative Efficiencies of Two De-aldehyding Procedures

Time	Official Method	Proposed Method
Min.	*Mg./cc.*	*Mg./cc.*
0	17.0	17.0
10	1.0	0.3
30	0.4	0.2
40	0.2	0.1
60	0.1	0.05
90	Trace	Trace
120	Trace	0

It was, of course, inevitable that resinification of some of the aldehyde should occur in that portion to which both aluminum and alkali had been added; nevertheless it is apparent that the reducing action of the metal is a material aid in speeding up removal of the aldehyde. The evidence appears convincing that the last traces of aldehyde bodies are removed with greater dispatch and convenience than by other procedures. It is these last traces which appear to be the troublesome factors in purifying ethyl alcohol for alkali-solvent purposes.

As a result of a series of determinations of saponification numbers of fatty oils with reagents prepared from ethyl alcohol, purified on the one hand by the silver oxide method (*4*) and on the other by the combined action of alkali and metallic aluminum, it was found that the use of ethyl alcohol treated by the latter procedure causes no significant differences. Pertinent data are recorded in Table II.

Table II. Comparison of Saponification Numbers

Oil	Alcohol by Silver Oxide	Alcohol by Aluminum and Potassium Hydroxide
Sesame	191.8	191.6
Cottonseed	194.9	195.0
Rye	176.5	176.8

A rough determination of the water content of a sample of alcohol before and after purification has shown that there is actually a partial dehydration of the product, the moisture content in this instance having been reduced from 7 to 3 per cent. This, however, is less important than that the proposed mode of procedure is efficient, economical of time and materials, and simple. It has been put to test with good success for the past year in the student laboratory of the Department of Chemistry and has never failed to produce an excellent product when the conventional methods proved wanting.

Throughout this study all distillations, both reflux and otherwise, were made in an all-glass apparatus (Figure 1) which had been constructed from a round-bottomed flask, a straight condenser, and a ground-glass joint, the latter being given a reverse bend. By merely turning the condenser from its upright position for reflux distillation through an angle of 180°, the system becomes a distillation outfit without the necessity of interrupting the heating.

Acknowledgment

Acknowledgment is made of the assistance given by Milford A. Cowley, who helped design and construct the all-glass apparatus used.

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A Laboratory Esterifying and Fractionating Apparatus

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The difficulty of duplicating exact plant conditions of large-scale processes in smaller laboratory equipment is well known in industrial research laboratories. In plant distillation processes the equipment used is usually capable of being operated over a very wide range of conditions. These variations include rates of operation, amounts of reflux, ratios between internal and external reflux, points at which reflux is returned to the system, points of crude feed to the system, selectivity in layer take off in the condensate, etc.

Many types of laboratory columns (*1*, *2*) and distillation set-ups (*3*, *4*, *5*) have been described in the literature for bringing about careful, precise fractionations. The use of such equipment is primarily for analyses by fractionation and cannot readily be applied to the duplication of general plant procedure.

The apparatus here described has been successfully used in the research laboratories of the du Pont company in connection with the manufacture of industrial solvents, plasticizers, etc., involving plant problems dealing with fractionation, vapor drying, and liquid-vapor countercurrent flow. As shown in the accompanying figure, it is fitted with a vapor line from the kettle, as well as a separate liquid reflux line to the kettle. The fractionating portion of the column is large to give capacity to the apparatus and is fitted with side auxiliary taps to provide various feed points, thermometer wells, or reflux return points along the column. The dephlegmator is adjustable in the cooling-water height as well as rate of cooling-water flow. The receiver is suited to take off either layer of a two-layer condensate and to return either layer partially or wholly to the kettle or to various points in the fractionating column. The fractionating portion of the column is well insulated to prevent the transfer of heat from the liquid and vapors in the column to the outside wall. This minimization of heat transfer from the column is very important in duplicating plant conditions where the transfer is very small. Experience with this apparatus has shown it closely to approach plant duplication.

Description, Assembly, and Operation

The over-all height of the apparatus as shown in the figure is approximately 111 cm. (44 inches) and it occupies about 0.09 square meter (1 square foot) of bench space. It is assembled from three major parts: kettle, column, and re-

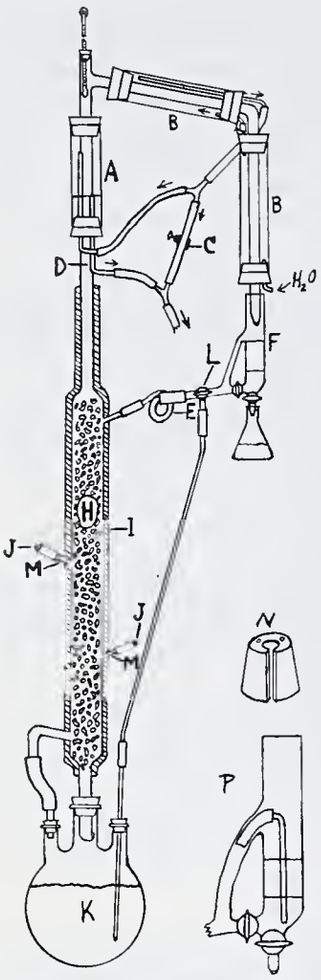

FIGURE 1. ASSEMBLED APPARATUS

A. Dephlegmator
B. Condensers
C. Screw clamp
D. Sliding H_2O outlet
E. Liquid trap
F. Separating receiver
H. Fractionating medium
I. Lagging
J. Solid stops
K. Kettle
L. Three-way stopcock
M. Auxiliary taps
N. Lower stopper for dephlegmator
P. Receiver, showing siphon for returning lower layer to column

ceiver. All three can be made of Pyrex glass. The column is lagged by wrapping tightly first with asbestos rope and then with tape to add compactness and durability to the insulation. *I* indicates the portion of the column lagged. The dephlegmator *A* is made by boring and cutting a No. 9 rubber stopper, as shown in the small inset *N*. The small holes are for water inlet and outlet lines. The upper stopper is cut in the same way except that only one small hole is needed, which acts as an air passage. A strip of medium thick pyroxylin sheeting is cut 12.5 cm. (5 inches) wide and about 20 cm. (8 inches) long. This is rolled to approximately the size of the dephlegmator, tied in this position with string, and placed in an oven at 90° C. for one hour. Upon cooling and untying it will be found to have assumed the rolled form. The rubber stoppers are then put in place on the column and the slits closed by drawing fine wire around the stopper at two or three points. The pyroxylin roll is then put in place around the stoppers and sealed by pouring acetone between the overlapping surfaces and holding tightly in place for a few seconds. The pyroxylin shell will seal itself firmly. Further to insure tightness and strength to the dephlegmator all joints are covered with a generous coating of du Pont household cement. The water inlet and outlet are formed of glass tubing, as indicated in the drawing. The outlet tube, although it must fit water-tight, should be loose enough to permit it to slide up and down through the rubber stopper, as this is an adjustable feature of the dephlegmator.

The upper condenser is constructed in the same manner as the dephlegmator, except that the upper rubber stopper does not have an air-vent hole and the stoppers do not need to be slit, as they can be moved into position over the arm of the column.

The lower condenser may be fitted with a glass shell which is slipped with the rubber stoppers over the end of the column arm. The water inlet is through the lower stopper, while the outlet is through the upper stopper. The condensers should be constructed to cover as much of the column side arm as possible.

The assembly of the dephlegmator and upper condenser may be greatly simplified by having the column made with a ground-glass joint in the small part of the column and another in the horizontal section of the side arm. This will, of course, increase the cost of the column. A still further improvement with additional expense would be to have condensers blown on the side arm during the manufacture of the column.

Having assembled the dephlegmator and condensers, the column is filled with a fractionating medium, such as glass beads or coarse Carborundum, to the point where the restriction in its larger diameter begins. Care must be taken not to fill the column too full, as an obstacle in the smaller upper section will cause flooding and greatly decrease the capacity of the column.

The glass receiver is connected with the column, as shown in the figure, through the liquid trap *E*. The trap is made of 0.16-cm. (0.06-inch) capillary glass tube with an outer diameter of 0.63 cm. (0.25 inch). Such a trap is strong and will not retain appreciable liquid.

The various connections of rubber tubing, shown in the figure, are made to complete the assembly of the apparatus. It should be noted that the condenser outlet fits loosely in the receiver, so that pressure does not build up in the apparatus during operation.

In operating the still as a drying column, the receiver is set so that the separating chamber will fill with the condensate. When the chamber is full, the oil, or water carrier, will flow through the return line either to the column or directly to the kettle, depending on the setting of the three-way stopcock *L*. The water settling out in the separating chamber may be drawn off through the bottom as it collects. If the water carrier used should be a liquid heavier than water and forms a lower layer, the siphon shown in the inset *P* may be used. It consists of a small-bore L-shaped glass tube with a short piece of rubber tubing attached, and is placed in the receiver as illustrated. The piece of rubber tubing should be of a size to fit snugly, but not tightly, in the upper return line of the separating receiver. The siphon is primed by allowing the receiver to fill beyond the upper outlet. After once started it will maintain a definite upper level in the receiver and will remove only the lower layer.

The internal reflux or dephlegmation of the column may be regulated by regulating the amount of cooling water flow through the dephlegmator as well as the height of cooling water maintained in the dephlegmator. The screw pinch clamp *C* adjusts the flow of cooling water, while any desired height of cooling water in the dephlegmator may be obtained by the proper setting of the sliding outlet *D*.

SUMMARY

The distillation apparatus described is extremely versatile in its application. It is designed primarily to duplicate in the laboratory the conditions of large plant stills used in esterification, rectification, and drying processes as carried out in the chemical industries. It is of simple construction, easily operated, requires very little space, and is suited to work with practically all commercial solvents.

ACKNOWLEDGMENT

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Determination of Amino Acids and Related Compounds in Honey

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Because of interference of reducing sugars with formation of the characteristic color, the ninhydrin test cannot be used for the detection or the determination of amino acids and related compounds in honey. A method for determining amino acids and related compounds in the presence of reducing sugars is proposed which is based on precipitation with Neuberg's reagent (mercuric acetate + sodium carbonate). The precipitated mercury amino compounds are separated by filtration or centrifugation, washed, and the free acids recovered by decomposing the mercury compounds with hydrogen sulfide. The ninhydrin test is then applied to the resulting solution.

The application of the method to a number of honey samples (after removal of proteins and other colloidal material) showed small amounts of amino acid nitrogen to be present in every case.

When honey is utilized for purposes that require heating to relatively high temperatures, as in the manufacture of candy or for baking, it is found to undergo decomposition at temperatures somewhat below that of a mixture of dextrose and levulose of approximately the same concentration as honey. In other words, the caramelization temperature of honey as a rule is lower than that of commercial invert sugar. This low caramelization temperature of honey must also be reckoned with when honey is heated to retard granulation or prevent fermentation. Often such treatment tends to impair the flavor, as well as to produce some discoloration due to slight caramelization.

From tests conducted in this laboratory on honeys of different floral sources, considerable differences were found to exist among the various types with respect to their tendency to caramelize when heated. The low caramelization temperature of honey, as pointed out in a previous communication (*3*), is due partly to the presence of certain colloidal substances. The colloids isolated from honey were found to decompose to an appreciable extent when subjected to temperatures above 50° C. Honey that had been treated so as approximately to free it from colloids, however, was still found to be more subject to caramelization on heating than commercial invert sugar. Apparently then, other nonsugar substances present in honey besides colloids are responsible for its low caramelization temperature.

In a recent paper (*5*) it was shown that, in addition to proteins, nitrogenous compounds of amino-acid character are present in honey. Since reducing sugars apparently interfere seriously with the development of the characteristic color of the ninhydrin reaction, it was found necessary to separate the amino acids from the reducing sugars of the honey before application of the test.

Because the presence of any considerable quantities of amino acids in honey would tend to promote darkening in color, due to melanoidin formation resulting from the reaction between amino acids and reducing sugars of the honey, it was thought that differences in behavior of various types of honey with respect to caramelization might be due, partly at least, to variations in the amino acid content.

With this consideration in mind, an attempt has been made to refine the precipitation method previously reported for the detection of amino acids in honey so that it would serve as a quantitative method for the estimation of amino acids and related compounds. Such a method might also be useful for the determination of these compounds in other saccharin products similar in composition to honey.

In 1922 Riffart (*6*) made a thorough investigation of the ninhydrin test as a quantitative method for determining amino acids and related compounds. He found the method to be suitable for detecting small amounts of amino acids colorimetrically, in some cases in a dilution of 1 to 340,000. He also studied the action of the reagent on a number of substances that might interfere with the reaction.

Ambler (*1*) has worked out a simplified modification of Riffart's method and applied it to the determination of amino acids and related compounds in sugar products. The presence of sucrose does not affect the reaction, and the method is very satisfactory and reasonably accurate. Attempts to apply the ninhydrin test directly to honey solutions, however, resulted in the development of a deep brownish red color, and upon dilution no characteristic violet color was obtained. In a recent article Ambler and Snider (*2*) showed that the presence of reducing sugars in appreciable amounts—namely, more than 1 mg. of levulose or 10 mg. of dextrose—altered the typical violet color of the reaction mixture, and in cases where larger quantities of these sugars were present the characteristic color did not appear at all on dilution.

Since honey consists largely of dextrose and levulose, detection of amino acids cannot be carried out by application of the ninhydrin test directly to the honey itself, and some means of separating the amino acids from the sugars is necessary. By precipitation of the amino acids from a honey solution with Neuberg's reagent (mercuric acetate + sodium carbonate), and subsequent treatment to remove the free acids, a good ninhydrin test was obtained, showing that failure to obtain positive tests in the above case was due to interference of reducing sugars.

The procedure for precipitating amino acids with mercuric acetate and sodium carbonate according to Neuberg and Kerb (*4*) is carried out as follows:

> To the amino-acid solution made alkaline with sodium carbonate is added a 25 per cent solution of mercuric acetate. More sodium carbonate is added as necessary to neutralize the acetic acid set free, and addition of mercuric acetate is continued until it causes a permanent yellow coloration of mercuric oxide. The precipitation is completed by addition of 5 to 8 volumes of 98 per cent alcohol. The precipitate is filtered, suspended in water, and the mercury removed by treatment with hydrogen sulfide. The amino acids in the resulting solution can then be detected by use of the ninhydrin test.

Application of the procedure of Neuberg and Kerb to a number of honey solutions gave good tests for amino acids in each case. Before applying the test, the honey solutions

were freed from proteins and other colloidal matter by use of bentonite.

Vondrák (7) has made a study of the precipitation of amino acids from sugarhouse products. He modified the method of Neuberg and Kerb somewhat for his work. He used normal mercuric acetate and sodium carbonate solutions, and showed that by using the correct proportions of each reagent he could practically precipitate quantitatively a known amount of amino acid from a sugar solution. He also found that the relative proportions of the two reagents necessary to produce complete precipitation varied somewhat, depending on the particular amino acid under investigation.

Precipitation of Amino Acids from Invert Sugar Solutions

Since the composition of invert sugar closely approximates that of honey, known quantities of amino acids were added to pure invert sugar solutions and recovery of the amino acids attempted by precipitation as mercury compounds. Several different amino acids were used for these tests. Apparently, added quantities of amino acids can be completely recovered from invert sugar solutions, provided the proper conditions for precipitation are observed. Table I shows the effect of varying the amounts of sodium carbonate and mercuric acetate on the completeness of precipitation of known quantities of aspartic acid from an invert sugar solution. The precipitations were carried out in 20-cc. portions of invert sugar solution containing 1.0 mg. of added amino nitrogen in each. After filtration and washing, the mercury precipitates were decomposed with hydrogen sulfide to liberate the acids and the ninhydrin test was applied to the resulting solutions.

Table I. Effect of Varying Amounts of Reagents on Completeness of Precipitation of Aspartic Acid from Invert Sugar Solutions

Sodium Carbonate[a]	Mercuric Acetate[a]	Color of Precipitate	Amino Nitrogen Added	Amino Nitrogen Recovered	Recovery
Cc.	*Cc.*		*Mg.*	*Mg.*	%
2.0	2.0	White	1.000	0.625	62.5
3.0	3.0	White	1.000	0.875	87.5
4.0	4.0	Faint pink	1.000	1.000	100.0
5.0	5.0	Pink	1.000	1.000	100.0

[a] 1.0 *N* solution.

Although complete recovery of aspartic acid from invert sugar solutions was obtained it was found in case of certain of the other amino acids that complete recovery was not possible by this simplified procedure. Neuberg and Kerb (4) have pointed out that the mercury compounds of some of the amino acids have appreciable solubility in water, so that the acids are incompletely precipitated from a water solution. To overcome this they precipitated the acids from an alcoholic medium, in which the mercury compounds are less soluble. As was found later, the addition of alcohol is necessary in order to obtain complete recovery of mixtures of amino acids from invert sugar solutions.

A number of these difficulties were also encountered in carrying out the precipitation and subsequent recovery of the amino acids. Filtration of the mercury precipitate is slow, and it is difficult to wash it free of sugars without use of excessive quantities of water. This difficulty was overcome by use of centrifugation. The precipitation of mercury with hydrogen sulfide was also troublesome, colloidal mercuric sulfide being almost invariably formed. This was overcome by addition of a small quantity of hydrochloric acid, and precipitating while hot. Centrifugation was also used for removing the precipitated mercuric sulfide.

The inclusion of these modifications in the method for recovering amino acids from invert sugar solutions appears to give virtually complete precipitation and recovery of the added amino acids. Alcohol is added until a concentration of about 80 per cent is obtained in the solution, from which the acids are precipitated as mercury compounds. Four different amino-acid solutions were prepared of such a concentration that each cubic centimeter contained 0.025 mg. of amino nitrogen. A fifth solution was prepared consisting of equal proportions of the first four amino-acid solutions. Twenty-five cubic centimeters of each solution were added to 25-gram portions of 80 per cent invert sugar solution, and precipitation and subsequent determination of the acids carried out as described in the method finally adopted for use with honey. A blank determination was also made using 25 grams of the invert sugar solution and 25 cc. of water. Complete recovery of the added amino acids was obtained in every case. With some of the individual amino acids the shade of color of the ninhydrin solution differed from that of the standard, being slightly bluer with glycine and alanine, and slightly redder with glutamic acid. The color developed by the mixed acids, however, matched the standard almost exactly.

It is recognized that certain amino acids such as cystine do not develop a color with ninhydrin, so that any cystine present in a mixture of amino acids would not be estimated by this method. This is an inherent difficulty of the ninhydrin method of determining amino acids, however, and does not concern the precipitation and separation of amino acids from reducing sugars.

In order to determine the shade and intensity of colors developed by various individual amino acids when treated with ninhydrin, solutions containing equivalent concentrations of alanine, glycine, valine, leucine, glutamic acid, cystine, phenylalanine, tyrosine, and asparagine were tested by the ninhydrin method, and the colors compared using aspartic acid standards. The nitrogen in each case, with the exception of cystine, was quantitatively accounted for. Cystine gave no color on application of the ninhydrin test. A mixture consisting of equivalent proportions of the nine solutions was tested in the same manner. Ninety-two per cent of the amino nitrogen present was accounted for. The cystine present in the mixture apparently accounts for this low recovery of nitrogen. Very slight differences in the shade of color of the ninhydrin solution compared with the aspartic acid standards were observed for some of the individual amino acids. The mixture of nine acids, however, gave a shade which matched the aspartic acid standards almost exactly.

Method

In view of the foregoing results, the following method has been used for the determination of amino acids and related compounds in honey:

Twenty-five grams of protein-free honey[1] are weighed, dissolved in 25 cc. of water, and the solution mixed with 200 cc. of 95 per cent alcohol. The precipitation is carried out by adding alternately from burets 1-cc. portions of 1.0 *N* sodium carbonate and freshly prepared 1.0 *N* mercuric acetate. After each addition the solution is tested with bromothymol blue paper, and if the solution reacts acid, an additional 1-cc. portion of sodium carbonate is added. The alternate addition of carbonate and acetate is continued until the precipitate assumes a distinctly yellow or orange color, and shows a tendency to settle. The final mixture should react slightly alkaline. The precipitate is separated by centrifuging the mixture, pouring off the super-

[1] The honeys used in these tests had been clarified by treatment with bentonite. Tests made on bentonite-treated honeys showed that proteins were removed by the treatment. While other means of removing the proteins could be employed, bentonite treatment is recommended because of its simplicity. For treatment with bentonite, a 1 to 1 honey solution is treated with a 5 per cent bentonite suspension, 1 volume of bentonite suspension being used for 10 to 15 volumes of honey solution.

natant liquid and washing several times with 20-cc. portions of 80 per cent alcohol, the supernatant liquid being poured off after each centrifuging. Three such washings are usually sufficient to remove practically all the sugars. The washed precipitate is then suspended in the centrifuge tube in 50 cc. of water, and 5 drops of concentrated hydrochloric acid are added. The tube is immersed in a beaker of boiling water, and hydrogen sulfide passed in for 10 minutes, during which the beaker of water is kept near boiling temperature. The precipitate is centrifuged and the supernatant liquid poured through a 7-cm. filter paper. The precipitate is stirred with 20 cc. of water, 2 drops of concentrated hydrochloric acid are added, and hydrogen sulfide is passed in for a second 10-minute period as above, in order to insure complete decomposition of the mercury compounds. The precipitate is centrifuged and the liquid poured through the same filter. The precipitate is stirred up with two 20-cc. portions of water, 1 drop of concentrated hydrochloric acid being added each time to prevent formation of colloidal mercuric sulfide, and centrifuged as before. The filtrate and washings are concentrated *in vacuo* to about 15 cc. and transferred to a small beaker. Two drops of phenolphthalein are added and dilute sodium hydroxide added drop by drop until the solution is very faintly alkaline. Very dilute hydrochloric acid is then added until the solution is just colorless. At this point it should react neutral to bromothymol blue paper. The solution is made up to 25 cc., and a 2-cc. aliquot representing 2 grams of the original sample is used for determination of amino acids by means of the ninhydrin test. The ninhydrin test is conducted according to the directions of Ambler (*1*), using aspartic acid as a standard.

The above procedure was used for the determination of amino acids and related compounds in ten samples of honey representing various floral types. Results of these tests are shown in Table II. The amount of amino nitrogen present varied between 0.0024 and 0.0066 per cent. Buckwheat and tarweed honeys showed relatively high amino-acid nitrogen values, whereas white clover, sage, and orange were among those showing the lowest values. In a general way a correlation was found to exist between the amount of amino nitrogen as determined above and the tendency of the honey to caramelize on heating, the observations being made on honeys from which colloids had been eliminated. The amounts of amino nitrogen found by the above procedure account for only part of the nitrogen present in honey after proteins and other colloidal materials are removed. Owing to the small amounts present, no attempts were made to isolate individual amino acids from the mixtures resulting from the mercury precipitation process. Portions of the solution, however, when treated with small amounts of glucose and warmed on the steam bath darkened very quickly and soon assumed a very dark brown color, at the same time emitting an odor typical of that usually associated with malanoidin formation. A portion of the solution itself and a portion of glucose solution when heated separately in the same manner did not discolor.

Table II. Amino Acid-Nitrogen Content of Honeys of a Variety of Floral Types

Predominant Floral Source of Honey	Amino Nitrogen	Amino Nitrogen (Dry basis)
	%	%
Buckwheat	0.0050	0.0062
Sumac	0.0025	0.0030
Catsclaw	0.0022	0.0027
Orange	0.0020	0.0024
Tarweed	0.0055	0.0066
Hawaiian honeydew	0.0045	0.0056
White sage	0.0020	0.0024
Alfalfa	0.0045	0.0053
Sourwood	0.0025	0.0029
White clover	0.0022	0.0026

While the results outlined here do not account for nearly all of the nitrogenous constituents of honey that are present as compounds of relatively small molecular weight, they show the existence of compounds of amino-acid character, and the influence they exert on certain properties of honey. A further study is being made of the nitrogenous constituents of honey.

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Effect of Alkali Treatment on the Yield of Lignin

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Several investigators (*2*, *3*, *6*, *7*) have reported that the treatment of wood with dilute alkali removes a portion of the lignin. Their experimental work was done, however, before it was found that rigid control of temperature and time was required for an accurate determination of lignin (*4*, *5*, *8*). It was desirable, therefore, to repeat, with proper control of time and temperature conditions, the experiments previously reported in order to determine whether the decrease in lignin yield after alkali treatment was the result of the removal of lignin or of some carbohydrate material readily charred and made insoluble by the action of 72 per cent sulfuric acid. There was also the possibility that a part of the extraneous matter was not removed by the neutral solvents commonly used in the analytical method, that this residue was insoluble in the sulfuric acid and was removed by the alkali treatment, thus lowering the apparent lignin yield. Cohen and Dadswell (*1*) have found that certain eucalypts contain large quantities of such extraneous material and that the lignin obtained after extraction with neutral solvents only was contaminated with extractives. In the determination of lignin in these woods they found it necessary to extract with dilute alkali in order to obtain any reasonable figures and they suggest that extraction with alkali precede the lignin determination in all cases. They state that the slight decreases observed by them in lignin yield from hemlock and spruce after preliminary treatment with alkali are also due to extraneous materials and not to the removal of true lignin.

When only small differences in lignin yield are caused by alkali extraction it is difficult to decide from the lignin yields alone whether the differences are due to the actual removal of lignin or to the removal of extractives that would otherwise

be segregated with the lignin. It is only by determining whether there is a change in the chemical composition of the lignin residue that any satisfactory conclusion can be reached.

The plan of the present work, therefore, included the determination of the lignin by the more accurate new methods (*5*) and the determination of the methoxy content of the isolated lignin for evidence of change in chemical composition.

Experimental

Air-dried maple sawdust was used for this work. It was extracted in a special metal extractor with hot alcohol-benzene mixture (1 to 2) for 48 hours, dried to remove the benzene, and then extracted in the same extractor with hot water. The total loss by alcohol-benzene and water extractions was 13 per cent of the weight of the oven-dry sawdust. The first alkali treatments were made according to the method used by Cohen and Dadswell (*1*) in which the sawdust was treated with a small volume of alkali (100 cc. to 2 grams). The loss of lignin in these treatments was roughly proportional to the amount of solution used. Accordingly, it was necessary to increase the volume of alkali until variations due to differences in volume would be small. A volume of 1200 cc. of alkali for each 6 grams of sawdust gave results that checked within the limit of error.

Two temperatures have been used most commonly by various investigators for treatment with alkali—namely, room temperature (about 22° C.), and on a boiling water bath (about 95° C.). A series of treatments using 0.5, 1.0, 5.0, and 10.0 per cent alkali were made at each of these temperatures.

The sample, which comprised 5 to 6 grams of maple sawdust, was weighed into a flask and 1200 cc. of the alkali solution were added. One group of samples was allowed to stand 24 hours at a temperature of 22° C. and the other was heated for 2 hours at a temperature of 95° C. in a water bath, after which a supernatant liquor was decanted through an alundum crucible. Cold water was added to both groups and removed by decantation until the filtrate was practically neutral. This treatment was followed by washing with hot water, neutralizing the absorbed alkali with 5 per cent acetic acid solution, and another washing with hot water until acid-free. The sample was then washed into an alundum crucible and dried at 105° C., after which the loss in weight was determined.

The lignin was determined according to the modified procedure in use at the Forest Products Laboratory (*5*); the methoxyl was determined by the standard method (*9*).

Discussion

The results shown in Table I confirm the previous observations that lignin was removed by alkali treatment. The lignin removed had the same percentage content of methoxyl as that remaining; therefore the apparent loss of lignin was not due to nonlignin substance of the wood carried over into the lignin residue because of its insolubility in 72 per cent sulfuric acid. Had there been a nonlignin substance in the lignin isolated from untreated wood, there should have been an increase in methoxyl after extraction.

A comparison of the methoxyl content of the treated wood with the methoxyl content of the isolated lignin shows that, after the original treatment with alkali which would remove all methoxyl attached as in an ester or as in pectin, the ratio is constant. The difference between the methoxyl content of the treated wood and that of the lignin isolated from it may be due to a methyl-glucoside-type linkage which is stable in alkali but hydrolyzed by acid.

The values given in Table I show that there is a close relationship between the total loss in weight and the loss in lignin. This same ratio may not be characteristic of other varieties of wood. The fact is established that, if the isolated lignin is to be representative of and equal to the native lignin, the wood must not be treated with alkali of any concentration before the isolation or determination is made.

Table I. Loss by Alkali Treatment and Determinations of Lignin and Methoxyl Using Treated Maple Sawdust

Alkali Used	Alkali Soluble	Lignin	MeO from Isolated Lignin	MeO in Isolated Lignin	MeO in Treated Wood
%	%[a]	%[a]	%[a]	%	%[a]
Extraction at 22° C. (1200 cc., 24 hours)					
0.0	0.0	20.9	4.35	21.0	6.5
0.5	8.0	19.2	3.84	20.0	4.9
1.0	10.4	18.7	3.75	20.0	4.6
5.0	19.0	17.7	3.62	20.3	4.6
10.0	19.2	17.2	3.60	20.9	4.6
Extraction at 95° C. (1200 cc., 2 hours)					
0.0	0.0	20.9	4.35	21.0	6.5
0.5	14.3	17.5	3.55	20.0	4.5
1.0	17.4	17.3	3.47	20.0	4.3
5.0	26.0	16.3	3.34	20.4	4.1
10.0	30.0	15.5	3.20	20.8	3.9

[a] Percentages are expressed on the weight of the original sawdust when oven-dry.

Summary

Previous observations on the decrease in the yield of lignin from wood as a result of extraction with dilute alkali have been confirmed using a more accurate method of lignin determination.

The material removed from wood by alkali treatment is really lignin and not insoluble residues of extractives. This is shown by the constant methoxyl content of the lignins before and after alkali treatment of the wood.

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China Adds Three Plants to Industrial Program. Plans for a paper mill, a rayon factory, and an industrial alcohol plant are under consideration by the Chinese National Government, according to the Department of Commerce.

The paper mill is to be erected in coöperation with leading paper consumers of Shanghai and the government will advance funds to assist in getting the enterprise into operation. The pulp mill is to be located in Hangchow, in Chekiang Province, and the factory for manufacturing finished paper, in Shanghai A rayon manufacturing plant is also planned by the government, it is understood, though no definite plans have been announced. It is expected that the plant will be large enough to supply the demand for rayon in China, but will not affect the country's silk industry. The Chinese Government also intends to establish a large factory at Shanghai for the manufacture of industrial alcohol.

Value of Electrical Methods for Estimating the Moisture Content of Wheat

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THE standard method for the determination of moisture in wheat is the Brown Duvel distillation procedure (*4*). This method is the only official moisture test recognized under the United States Grain Standards Act for the grading of grain. However, because it is empirical and is affected by many variables, close checking between laboratories is frequently difficult to secure. In addition, the test is time-consuming and requires the constant attention of the operator. When it is necessary to make many moisture tests for grading wheat or for mill control work, the Brown Duvel method leaves much to be desired, as regards both accuracy and speed. Another method which is preferred by many mill laboratories, although it has no official sanction, consists in grinding the wheat and conducting on the ground wheat sample the official method for the determination of moisture in flour (*2*). The difficulty with this procedure is that in the case of wheats with higher moisture contents (above 14 per cent) there may be a loss of moisture by evaporation due to the handling and grinding previous to weighing. In addition, in the case of wet wheats there is often considerable sticking in the burrs of the grinder and the heat generated during the grinding causes a loss in weight. The oven method itself, if one were sure that no gain or loss in moisture had occurred during grinding, gives very consistent results. A quicker method which would eliminate the grinding of samples and still give accurate and closely agreeing results is, therefore, much to be desired.

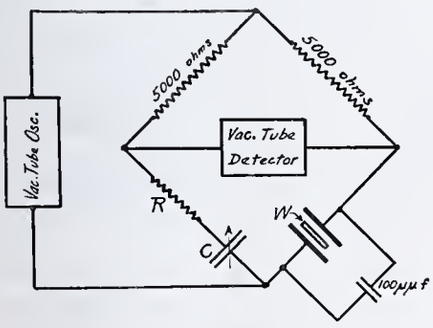

Figure 1

Electrical methods as a means of estimating the water content of grain were suggested several years ago (*5*, *13*). None of these methods, however, found commercial application. Recently several devices have appeared on the market for measuring the moisture in wheat which depend not upon a direct measurement of the water contained in a given sample but upon the effect of the water on certain electrical properties of the wheat. Among these devices are the Burton-Pitt apparatus, the D-K Schnell Wasser Bestimmung Apparat, the Berry dielectrometer, and the Tag-Heppenstall moisture meter (*3*, *6*). Several articles describing the use of such equipment have also appeared (*7*, *8*, *9*, *11*). These instruments give readings based on the electrical conductivity, the dielectric capacity, or complex combinations of these two properties which, by means of an empirical chart, are correlated with the moisture content of the wheat. Since the measurements are not direct determinations of the amount of water, it is essential to establish whether a given weight of water added to a given weight of wheat will invariably produce the same changes in the electrical characteristics of the wheat or whether the electrical properties depend also, in a significant way, upon other factors. Such factors might be the variety, class and grade of wheat (for example, whether hard red spring, durum, or soft red winter), the condition of the wheat (whether frosted, bin burnt, or damaged), the length of time between the addition of water and the measurement, the manner in which the wheat sample is placed in the container, the temperature, and numerous other possible variants.

The apparatus and experiments now to be described were devised for the purpose of investigating some of the fundamental factors underlying the estimation of moisture in wheat by electrical methods.

Description of Apparatus

A parallel plate condenser, between which a thin, hard rubber cell could be inserted, was connected in one arm of a General Radio shielded capacity bridge as shown at *W* in Figure 1. In the measuring arm of the bridge was connected a General Radio precision variable air condenser at *C*, and an 11,000-ohm decade resistance box, *R*, built integral with the bridge box. In shunt with the parallel plate condenser, *W*, a 100-micromicrofarad fixed air condenser was connected for the purpose of increasing the current through the bridge and thereby increasing the sensitivity of adjustment for bridge balance. To indicate balance a Western Electric four-stage vacuum-tube amplifier-voltmeter was used. Current for the bridge was supplied by a Western Electric adjustable-frequency vacuum-tube oscillator. Suitable precautions were taken to eliminate the effect of variable stray capacities on the measurements.

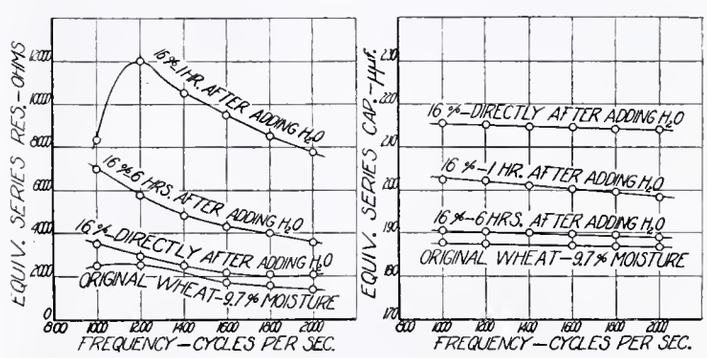

Figure 2

The inside dimensions of the flat cell, *W*, were 1.25 cm. by 7.5 cm. by 9.3 cm., so as just to accommodate a 50-gram sample of wheat. The cell was fitted by means of guides between the plates of the condenser so as always to occupy the same position after insertion.

Preparation of Samples

The samples used in this investigation were made up from the following classes of wheat: hard red spring (Marquis), hard red winter (Kansas), durum (Amber and Red), and western white (Sonora). Most of the samples originally contained between 8 and 10 per cent moisture. All tests by

the Brown Duvel distillation method were made in duplicate on a gas-heated apparatus in strict accordance with the official directions, except that the flame was extinguished at 190° instead of 180° C., since it has been shown that by making this change the Brown Duvel results compare more favorably with the results obtained by the vacuum-oven test (*1*).

The initial moisture having been carefully determined, 250 grams of wheat were weighed into screw-top, moisture-proof metal sample cans of 1 quart capacity. Basing calculations on the amount of moisture originally present in the wheat, the number of cubic centimeters of water necessary to increase the moisture to any given amount was calculated. In each series of experiments, samples were made up ranging in moisture from approximately 8 to 20 per cent in steps of 1 or 0.5 per cent differences. Water was added from a Bureau of Standards buret directly to the sample, the top tightly screwed, the sample vigorously shaken and then allowed to stand at room temperature for 12 to 48 hours. At the end of this time determinations were made by the Brown Duvel method and at the same time readings were taken on a separate 50-gram sample using the electrical apparatus.

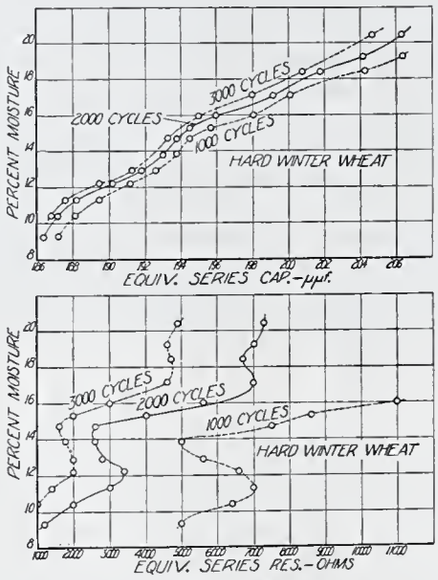

Figure 3

In most instances, the moisture content of the tempered samples as determined by the Brown Duvel procedure checked remarkably well with the theoretical moisture percentages as calculated from the amount of water added to a given weight of wheat of known moisture content.

In earlier experiments the 130° C. air-oven method was likewise employed to determine the moisture content of the wheats. This method gives consistently higher results than the Brown Duvel test, the difference between the two methods becoming less at the higher moisture levels. The authors were particularly interested in wheats having above 13 per cent moisture, since such samples showed more variable readings by all electrical measurements. In later work the 130° C. air-oven method was abandoned because it necessitated grinding, and the grinding of the wet samples before weighing resulted in a variable loss of water. All the moisture determinations cited in this paper were done by means of the Brown Duvel method.

Procedure

A 50-gram sample of the wheat to be tested was weighed and transferred by means of a special funnel to the hard-rubber flat cell, which was then inserted between the plates of the condenser. The bridge was then balanced for various frequencies and the total equivalent series resistance, R, and capacity, C (Figure 1), were recorded. On repeating the entire procedure, including the weighing of a new 50-gram charge, the readings of capacity and resistance could be duplicated very closely.

When wheat to which water has just been added is placed in the dielectric field of the condenser, the effective capacity and resistance vary with time. The results obtained with one sample are shown in Figure 2. The wheat in this case had originally a moisture content of 9.7 per cent and water was added in sufficient quantity to bring the moisture content to 16 per cent. Four sets of readings were taken, the first on the original sample containing 9.7 per cent moisture, one immediately after water had been added, and the two other readings 1 and 6 hours later, respectively. It will be observed that the increase in resistance immediately after adding water was comparatively small but rose on standing to a maximum and on further standing diminished to a final equilibrium value. The capacity, on the other hand, was largest immediately after adding the water and diminished steadily with time to its final equilibrium value.

This variation of measured capacity and resistance with time after adding water was also observed in a great number of wheat samples taken in various stages of the tempering process, prior to milling, in connection with the commercial operation of one of the larger mills of the Russell-Miller Milling Company. Obviously no consistent readings of capacity and resistance can be obtained unless a sufficiently long time has elapsed to establish equilibrium conditions or unless the time when the water was added is definitely known. It was also observed that wheat with a moisture content greater than about 14.5 per cent gave different values of R and C immediately after the sample was poured into the container and after it had stood about 5 minutes. On tapping the condenser, the initial value was restored and on further standing would reach the same final value as before. This procedure could be repeated as often as desired.

Figure 3 shows the variation of capacity and resistance of hard winter wheat for three different measuring frequencies—1000, 2000, and 3000 cycles per second—taken on samples which differed from each other in moisture content by approximately 1 per cent and in the range from 9 to 20 per cent. All the samples were allowed to stand in moisture-proof containers for 48 hours after the water was added and before the bridge readings were taken. It will be noticed that the curves for these frequencies are very similar, merely being shifted with respect to each other. Referring to the curve of equivalent series capacity, it should be emphasized that the wavy character of the curve is actual and not due to uncertainties in measuring the values of capacity. When the entire procedure of weighing the wheat, transferring to the flat cell of the condenser, and balancing the bridge was repeated, the reading could be checked to within less than 0.2 micromicrofarad.

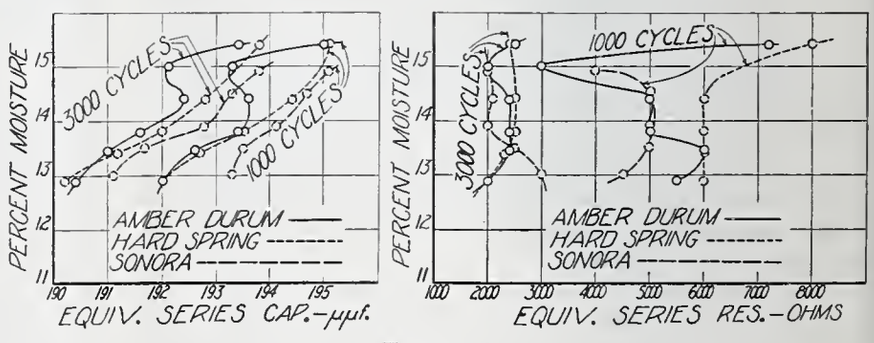

Figure 4

The curve bends over rather sharply at about 14.5 per

cent. This corresponds to a sharp increase in the equivalent series resistance of the sample for this moisture interval.

From the practical standpoint of attempting to predict the moisture content from the resistance curves, a glance at these graphs will show that one must surmount the difficulty of having to distinguish for a given series resistance—for example, 3000 ohms—between three different points on the appropriate curve. This, coupled with the fact that the resistance varies so rapidly and erratically with the moisture content, makes the prediction of moisture from these curves very uncertain. On the other hand, the capacity curves are fairly regular and it remains only to establish whether the curves are valid for varieties of wheat other than the kind for which they were determined.

The results obtained with three very different types of wheat are shown in Figure 4. The wheats analyzed were: Sonora, a California white wheat of low protein content; Marquis, a hard red spring wheat of high protein content grown in Montana; and an amber durum wheat of high protein content from South Dakota. In addition to the above-mentioned wheats, other classes such as red durum and hard winter were also tested and found to give similar results. From the curves given it is clear that both the resistance and the capacity values are very different for each of the varieties of wheat tested. Moreover, the curves for amber durum wheat exhibit the same value of capacity for three different percentages of moisture. No single curve, either of capacity or resistance, was found suitable for predicting the moisture content of all classes of wheat.

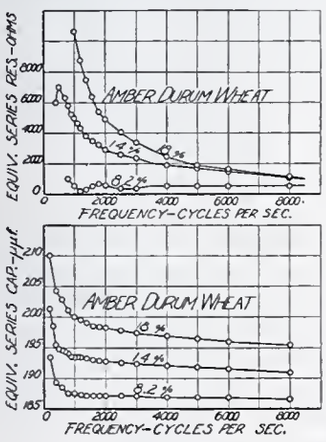

FIGURE 5

For the sake of completeness, the variation with frequency of the equivalent series resistance and capacity is shown in Figure 5. Amber durum wheat at three different moisture levels was investigated. No frequency was found which was better than those used in Figures 3 and 4 for correlating moisture content with the electrical properties.

DISCUSSION

Several possibilities suggest themselves as an explanation of some of the observed effects. The variation of effective capacity and resistance may be due, at least in part, to the presence of polar molecules in the wheat. Water by itself is well known to be electrically polar. The variation of capacity and resistance as a function of the time after water is added suggests very strongly that the electric polarity due to the added water is dependent not only on the amount of water but also upon the extent to which the water is "bound" by the components of wheat, thereby causing a change in the response of the polar molecules to the impressed electric field. The concept of water bound by biological materials and the difference in the physical properties of this bound water as compared to water in bulk has been extensively discussed by Gortner and others (*10*). In an organic material as complex as wheat it is very unlikely that the adsorbed water films are held uniformly throughout the structure of the wheat kernel. Moreover, it has been well established that a certain amount of the moisture contained in flour is not liberated by heating it at the boiling point of water even for relatively long periods of time (*12*).

Another electrical mechanism which probably plays a part in the variation of the resistance with frequency is that of dielectric absorption and the migration of ions back and forth through the dielectric under the influence of the external field. In support of the probability of such a mechanism may be cited the very peculiar behavior of the wheat samples containing moisture in excess of about 14 per cent. The resistance and capacity readings of such samples were altered when disturbed by mechanical shock. It is possible that such a change might be due to a disturbance of the coherence of the wheat particles and of the electric paths between them.

It should be emphasized that the resistance and capacity measurements obtained in this investigation and their variation with moisture content describe fundamental properties of wheat and are not dependent on the particular apparatus used to determine them. Other methods for obtaining resistance or capacity of whole wheat kernels would give similar results. It is therefore permissible to draw general conclusions as to the value of resistance and capacity measurements in estimating the moisture content of wheat.

CONCLUSIONS

It may be concluded from the results obtained on the measurement of the effective series capacity and series resistance of a condenser in which wheat formed the dielectric that:

1. The capacity and resistance readings depend not only on the amount of water present in wheat but also on whether sufficient time has elapsed to attain equilibrium after the addition of water.
2. Different varieties of wheat with the same moisture content may give different capacity and resistance readings.
3. Three samples of the same kind of wheat containing three different amounts of moisture may give identical readings of capacity or resistance.
4. It is unlikely that any of the devices for determining the moisture content of wheat by electrical means can give more than a rough approximation of the actual moisture content in the range and condition of greatest commercial interest.

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Platinized Silica Gel as an Oxidation Catalyst in Gas Analysis

I. Oxidation of Hydrogen and Carbon Monoxide

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IN THE analysis of those mixtures of gases that most commonly occur in technical practice, the determination of the majority of the constituents may be accomplished by the absorption of the gases in a chemical reagent. This method is not applicable to the determination of hydrogen or hydrocarbon gases of the methane series. In gas mixtures or gas residues that contain hydrogen and only one hydrocarbon of the methane series, both gases may satisfactorily be determined by burning the gases simultaneously in the combustion pipet (*4*), and measuring the contraction and volume of carbon dioxide formed. When hydrogen, methane, and ethane are present, the determination cannot be made (*5*) unless the hydrogen is first removed. For these reasons a satisfactory method of fractional combustion of hydrogen in the presence of hydrocarbons has long been sought and many different procedures have been suggested.

In technical gas analysis at the present time there is but one method in use for the fractional combustion of hydrogen, the copper oxide method in which copper oxide oxidizes the hydrogen (*1*). Although hydrogen, carbon monoxide, and methane can be determined by one combustion (*5*), the hydrogen and carbon monoxide may be oxidized by copper oxide at 300° C. without oxidation of the methane. Catalytic methods for the fractional combustion of hydrogen and carbon monoxide have been known since the work of Henry in 1825 (*3*), Hempel (*2*), and Nesmjelow (*6*) who used palladium on asbestos as the catalyst. Although used to a slight extent, it has been entirely replaced by the copper oxide method.

It is apparent that the unpopularity of this method is due to the very great care that must be employed in the analysis to secure check results, the low degree of selectivity of the catalysts, and the unwillingness of the analyst to prepare his own catalysts which might vary greatly in their degree of reactivity. If a commercial catalyst of uniform activity and a high degree of selectivity can be found, the method of catalytic oxidation has numerous advantages. For this reason the platinized silica gel produced by the Silica Gel Corporation for the oxidation of sulfur dioxide to trioxide was investigated as an oxidation catalyst in gas analysis.

Apparatus

The apparatus used in this investigation was the U. S. Steel Corporation gas apparatus (*7*). Mercury was used as the confining liquid and acid saturated sodium sulfate solution as the flushing liquid. The fuel gas buret furnished with the apparatus was used for all measurements. The platinized silica gel containing 0.075 per cent platinum was sized to pass 14 mesh and be retained on 20 mesh. About one gram of the catalyst was placed in a tube of the same dimensions as the standard copper oxide tube used with the apparatus. This catalyst tube replaced the copper oxide tube in the experiments using catalytic oxidation.

Determination of Hydrogen

A mixture of hydrogen, oxygen, and nitrogen was prepared and analyzed by the explosion method, using approximately 30-cc. samples. The procedure for using the catalyst tube was exactly the same as that used for the copper oxide method for determining hydrogen (*8*) using 100-cc. samples. In the first experiments, the catalyst tube was heated to a temperature of 125° C. It was found that after one passage of the gas through the tube most of the hydrogen was oxidized, and after four passes the hydrogen was completely removed and no further diminution in volume took place on further passage through the tube. In a second series of experiments the temperature was lowered and it was found possible to remove the hydrogen completely at a heater temperature of 80° to 85° C. The results are shown in Table I.

Table I. Determination of Hydrogen

(Gas mixture:[a] hydrogen, oxygen, nitrogen)

Analysis by Explosion Method									
Analysis	1	2	3	4	Av.	5	6	7	Av.
Hydrogen, per cent	16.3	16.5	16.1	16.3	16.3	14.4	14.5	14.5	14.5

Analysis by Catalyst Tube Method							
Analysis	1	2	3	Av.	4	5	Av.
Temperature of heater	125	125	125	..	80–85	90	..
Number of passes	4	4	6	..	6	4	..
Hydrogen, per cent	16.6	16.5	16.7	16.6	14.7	14.7	14.7

[a] 59 per cent oxygen in mixture.

Table II. Determination of Carbon Monoxide

(Gas mixture: carbon monoxide, oxygen, nitrogen)

Analysis by Explosion Method				
Analysis	1	2	3	Av.
Carbon monoxide, per cent	18.8	19.0	18.9	18.9

Analysis by Catalyst Tube Method			
Analysis	1	2	Av.
Temperature of heater	300	300	..
Number of passes	6	6	..
Carbon monoxide, per cent	19.0	19.0	19.0

Thus in the catalyst tube method it is not necessary to heat the tube to a temperature greater than 100° C. in order to oxidize all of the hydrogen, whereas in the copper oxide method a temperature of 300° C. is required. It was also found that the gas could be passed over the catalyst at a greater rate than with the copper oxide. A velocity of 30 to 50 cc. per minute was used, while a maximum rate of 20 cc. per minute is recommended with copper oxide.

In order to test the nature of the catalytic effect, a mixture of hydrogen and oxygen was passed over silica gel under the same conditions as with the platinized silica gel. No appreciable oxidation took place even at temperatures as high as 350° C., thus showing that the oxidation catalyst is the platinum supported on the silica gel.

Determination of Carbon Monoxide

A mixture of carbon monoxide, oxygen, and nitrogen was prepared and analyzed by the explosion method. When using the catalyst tube it was found necessary to raise the heater temperature to at least 300° C. in order to oxidize the carbon monoxide at the same rate at which hydrogen was oxidized. This is the same temperature used in the copper

oxide method, but the rate of flow is much faster than in that method. The results obtained by the explosion and catalyst tube methods check well and therefore indicate the suitability of the latter method. The results are shown in Table II.

Determination of Hydrogen in City Gas

The results obtained were next applied to technical gas analysis using the city gas, which is a carbureted water gas mixed with coke-oven gas. The usual method of analysis by absorption of carbon dioxide, illuminants, oxygen, and carbon monoxide was used, but hydrogen was determined by passage through the catalyst tube at a temperature of 100° C. Methane was not determined in all cases, as it required additional time. Analyses of the gas are given in Table III.

Table III. Analysis of Seattle City Gas

	%	%	%
Carbon dioxide	5.7	5.6	5.7
Illuminants	7.1	7.4	7.2
Oxygen	0.1	0.1	0.2
Carbon monoxide	13.4	13.1	12.9
Hydrogen	27.9	27.9	28.0
Methane and ethane	19.3	19.3	19.3 (approx.)
Nitrogen	26.5	27.0	26.7

A check of the hydrogen determination by the copper oxide method and the catalyst tube method was then made. The residues from four 100-cc. gas samples after absorption, containing only hydrogen, methane, ethane, and nitrogen, were mixed together to give a uniform mixture. Two copper oxide analyses and two analyses using the catalyst tube were made. The results are shown in Table IV.

Table IV. Determination of Hydrogen

	Copper Oxide Method		Catalyst Tube Method	
Analysis	1	2	1	2
Sample	53.7	86.1	49.3	53.9
Temperature of heater	300	300	100	100
Number of passes	..	..	8	8
Hydrogen, per cent	34.5	34.4	34.6	34.6

Thus it is seen that the catalyst tube method has as high a degree of accuracy as the copper oxide method. Though a very slightly greater amount of hydrogen was found by the catalyst tube method, it is believed that this is no error of this method. Rather the copper oxide tube may be at fault, for this reaction is a heterogeneous reaction in which the copper oxide is consumed, so that at the end of the oxidation but a very small amount of copper oxide may remain which may be insufficient to give an oxidation at an appreciable rate. The catalyst, however, is unchanged during the reaction and as long as an excess of oxygen is present the oxidation will go to completion on the catalytic surface.

Carbon Monoxide as a Catalyst Poison

After the catalyst was found successful in determining hydrogen from the residue after carbon monoxide had been removed, it was decided to try to oxidize the hydrogen without first removing the carbon monoxide. When the gas residue containing carbon monoxide, hydrogen, and hydrocarbons was passed through the catalyst tube at 100° C. no reduction in volume of the gas took place. The catalyst was found now to be inactive toward hydrogen-oxygen mixtures at 100° C., showing that poisoning of the catalyst had occurred. The same results were again obtained with a fresh charge of catalyst. Since carbon monoxide was oxidized when passed over the catalyst at a temperature of 300° C. an attempt was made to reactivate the catalyst by heating it to this temperature and passing air through the tube. This procedure caused an oxidation of the adsorbed carbon monoxide which was acting as the poison and the catalyst was found to be completely reactivated by this treatment, so that hydrogen could be determined as readily as before the poisoning had occurred.

Combustion of Hydrocarbons

A mixture of methane, oxygen, and nitrogen was prepared and passed over the catalyst at a temperature of 305° C. No carbon dioxide was found in the products. A hydrogen, methane, and oxygen mixture was prepared and passed over the catalyst at 100° C. for determination of the hydrogen. No carbon dioxide was found in the products. These data, taken with those of Table IV, show that hydrogen can be determined by catalytic oxidation at 100° C. in the presence of the hydrocarbons in city gas. An attempt was made to determine the possibility of oxidizing hydrogen and carbon monoxide together at 300° C. in the presence of the methane hydrocarbons in city gas. Some of the hydrocarbon residues of the city gas after carbon monoxide and hydrogen removal were passed over the catalyst with oxygen. At a temperature above 300° C. many passes gave only a fraction of a cubic centimeter of carbon dioxide. This seemed to indicate that the ethane and any other higher hydrocarbons which might be present were oxidized to some extent. The small amount of carbon dioxide formed eliminated the possibility of determining hydrogen and carbon monoxide in the gas residue by passage over the catalyst at 300° C. It was, however, found possible to oxidize both hydrogen and carbon monoxide at the same time at a catalyst temperature of 300° C., so that it should be possible to determine the composition of gases containing only hydrogen, carbon monoxide, and methane when the gas is mixed with sufficient oxygen and then passed through the catalyst tube at a temperature of 300° C. The oxidation of hydrocarbons is being studied further.

Advantages of Catalyst Tube Method

In the copper oxide method as the amount of hydrogen in the gas decreases, the rate of reaction falls off because of the decreased hydrogen and the fact that the surface of the copper oxide is reduced. The amount of hydrogen removed in the last few passes over the copper oxide is very small, so that the analyst may stop before all the hydrogen is completely removed, while with the catalyst tube the number of passes is considerably less, so that all hydrogen is removed. This fact makes the catalyst tube method much more rapid than the copper oxide method. Also the catalyst is unaffected by the reaction, while the copper must be reoxidized to copper oxide, a saving in time corresponding to one determination. The copper oxide soon loses its activity and must be discarded, while the platinized silica gel has an indefinite life. Though the catalyst is susceptible to poisoning by carbon monoxide at 100° C., it is easily restored to its original activity. The removal of carbon monoxide by absorption before the hydrogen oxidation offers no difficulty. With the copper oxide method the size of sample is definitely limited by the amount of copper oxide present to oxidize the hydrogen. However, with the catalyst a sample of any size may be taken, since oxidation is effected by the oxygen or air added and the mere presence of the catalyst is all that is necessary. The use of larger samples gives a greater degree of accuracy to the method. Lastly, the use of a standard commercial catalyst of uniform activity releases the analyst from the duty of preparing his own catalyst, which may have a variable activity.

Summary

1. Hydrogen is quantitatively oxidized by oxygen over a commercial platinized silica gel at a temperature of 100° C.
2. Carbon monoxide is a catalyst poison at 100° C. but is

oxidized at a temperature of 300° C., the catalyst being completely reactivated. Mixtures of hydrogen and carbon monoxide can thus be oxidized at 300° C.

3. Hydrogen in a hydrogen-hydrocarbon mixture may be determined by fractional combustion with oxygen by passing the gases from four to six times at a rate of 30 to 50 cc. per minute over the catalyst at a temperature of 100° C.

4. Further studies are being made on the extent of oxidation of methane and higher hydrocarbons under the conditions required for carbon monoxide oxidation.

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Volumetric Methods of Estimating Nitrites

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A LARGE number of procedures for the volumetric estimation of nitrites, or nitrous acid, are to be found in the literature. Because of the considerable difference of opinion as to the accuracy of these various methods, and the lack of a critical systematic study of them, a careful comparison has been made of a number of the procedures, in order to determine their relative values and see which might be expected to give accurate results when used by the average analyst under ordinary conditions.

Recalibrated precision volumetric ware and the best grade of c. p. chemicals were employed throughout the investigation. Conductivity water was used for all solutions, which were protected from light, blanks were run on all the reagents, and the usual end-point and temperature corrections were made. Standard solutions were made either from analyzed reagents of known purity, or the solutions were standardized against certified analytical standards, as, for example, Bureau of Standards sodium oxalate for permanganate. Standardizations, comparisons, and blanks were made under the same conditions as the determinations.

Samples of 50 to 100 mg. of sodium nitrite (10 to 20 cc. of a solution containing 5.0000 grams of recrystallized c. p. sodium nitrite per liter) were used for individual determinations.

Permanganate Methods

Direct titration of nitrite in strongly acid solution with potassium permanganate proved unsatisfactory. When the neutral nitrite solution was acidified a distinct odor was noticeable, indicating a loss of nitrous acid, and the results were invariably low. The process was also very slow because of gradual fading of the pink coloration near the end point. Decolorization was hastened by heating the solution to 50° C. near the end of the titration, but the loss of nitrous acid on acidifying the nitrite solution still introduced an error and the results were always low.

In an attempt to overcome the loss of nitrous acid when the solution was strongly acidified, permanganate was added to a neutral sodium nitrite solution until it became pink; it was then made slightly acidic and the titration was completed without further addition of acid. While the results obtained were nearer the theoretical than those with the preceding procedure, they were still low, giving a constant error of −1.4 per cent when 50 mg. of sodium nitrite were present, and a practically constant error of −2.2 per cent with 100 mg. of sodium nitrite. When the slightly acidic solution was strongly acidified just before reaching the end point (*6*), a nearly constant error of −1.3 per cent resulted with 50 mg. of sodium nitrite, and −1.4 per cent with 100 mg.

A procedure suggested by Adie and Wood (*1*) gave results with an average error of +0.1 per cent (procedure A, Table I). The amount of permanganate required to react with a measured quantity of the sample was determined approximately by adding standard potassium permanganate to a strongly acidified solution of nitrite. For the exact determination, standard permanganate solution was added to the neutral nitrite, diluted to 100 cc., to within 1 cc. of the amount found in the preliminary approximate analysis. Then 10 cc. of 6 *N* sulfuric acid were added and the titration was completed.

Lunge (*17*) claimed that if the titration process is reversed, so that the nitrite is added to acid permanganate, the nitrogen trioxide set free from every drop of the nitrite is immediately oxidized before it can decompose into nitric oxide and nitrogen pentoxide. On adding the nitrite solution to permanganate, 0.6 *N* with sulfuric acid, an average error of −0.4 per cent resulted (procedure B, Table I). However, decolorization of the permanganate takes place very slowly near the end point, and the large errors obtained in some of the determinations were probably due to the titrations being carried out too fast, with a consequent over-stepping of the end point. In order to hasten the decolorization near the end point and thereby shorten the time of titration, determinations were made with the permanganate heated to 30° to 40° C. as recommended by Lunge (*17*) at different rates of titration. The results obtained indicate the necessity of carrying out the titration slowly, especially near the end point, which still appears slowly in spite of the heating, although it is faster than at room temperature. When the titrations were carried out as fast as possible, the average error amounted to −0.5 per cent. At a moderate rate of titration the error decreased to −0.1 per cent, and when the titration was conducted very slowly near the end an average error of +0.1 per cent was obtained (procedure C, Table I).

Table I. Summary of Results of Satisfactory Methods

Procedure	Error: Maximum %	Minimum %	Arithmetical mean %	Average deviation from arithmetical mean %
A	+0.2	±0.0	+0.1	±0.1
B	−0.7	−0.1	−0.4	±0.2
C, fast	−0.7	−0.3	−0.5	±0.2
C, moderate	±0.6	±0.0	−0.1	±0.4
C, slow	+0.3	±0.2	+0.1	±0.2
D, 3–36% excess $KMnO_4$	+0.4	±0.0	+0.3	±0.1
D, 127–132% excess	+0.8	+0.4	+0.6	±0.2
E	+0.4	+0.2	+0.3	±0.1
F	+0.4	±0.0	+0.2	±0.2
G	+0.3	±0.0	+0.2	±0.1
H	+0.8	+0.1	+0.2	±0.2
I	−0.4	±0.0	−0.1	±0.2
J	+0.5	±0.0	+0.1	±0.2

The reaction may be hastened by adding the nitrite to an excess of acid permanganate which may then be determined with sodium oxalate, oxalic acid (*13*, *25*), or ferrous sulfate (*19*, *2*). This procedure also eliminates the necessity of a clean buret (required in Lunge's method) for each sample of nitrite. When sodium oxalate was used to determine the excess permanganate, the average error amounted to +0.3 per cent with from 3 to 36 per cent excess permanganate, and +0.6 per cent with about 130 per cent excess permanganate (procedure D, Table I). In these determinations the solutions containing the excess permanganate were heated to 90° C. before adding the sodium oxalate, and the temperature was not allowed to fall below 60° C. until the titration had been completed. When a large excess (130 per cent) of permanganate was present, a heavy precipitate was formed at about 60° to 65° C., on heating the solution. This was dissolved by the addition of a small excess of sodium oxalate. The titration was then completed by adding a slight excess of permanganate and titrating with sodium oxalate to the disappearance of the pink coloration. When only a small excess of permanganate was present, no precipitate formed while the solutions were being heated. However, in the determinations of the 100-mg. samples precipitates formed while the solutions were standing at 90° C., waiting for the initial buret readings to be made. An average error of +0.3 per cent resulted when ferrous ammonium sulfate was used to determine the excess permanganate at room temperature (procedure E, Table I). When the sulfate was added slowly a slight precipitate settled out, but when added rapidly no precipitate was formed.

The dissolving of the precipitates by excess reducing agents suggested the possibility of using first excess acid permanganate, then excess reducing agent, and finishing the titration with permanganate. Experiments demonstrated that such a method would work successfully, and a search through the literature showed that such a procedure had been reported by Kubel (*15*), Fresenius (*8*), and Laird and Simpson (*16*). Sodium oxalate (procedure F, Table I), ferrous ammonium sulfate (procedure G), and hydrogen peroxide (procedure H), were used as reducing agents. Each gave an average error of +0.2 per cent.

Experiments were made to determine the stability of the standard nitrite, hydrogen peroxide, ferrous ammonium sulfate, and sodium oxalate solutions, and the standard potassium permanganate was restandardized several times during its use. The sodium nitrite solutions seemed to be quite stable. No change could be detected in solutions which had been made up for from 4 to 5 weeks. In a month the normality of the ferrous ammonium sulfate (containing 5 cc. of concentrated sulfuric acid per liter) had decreased from 0.1014 *N* to 0.0914 *N*, while that of the sodium oxalate had decreased from 0.0995 *N* to 0.0990 *N*. No change could be detected in a solution of hydrogen peroxide (made up in 1.0 *N* sulfuric acid) which had stood for 3 weeks. A solution of standard potassium permanganate which had been prepared by dissolving the salt in redistilled water, boiling the solution gently in a covered beaker for about 20 hours, filtering through washed ignited asbestos, and diluting with sufficient redistilled water to make the solution tenth normal showed no change in normality during the 8 months it was used, and there was no trace of a precipitate in the bottle when it was emptied.

Iodometric Methods

Two of the iodometric methods tried proved satisfactory. Both, however, involved oxidation of nitrite with excess acid permanganate and determination of the excess permanganate iodometrically. The method given by Griffin (*10*), in which the nitrite is heated to boiling with standard permanganate, acidified, let stand 10 minutes, and then cooled before adding potassium iodide, gave an average error of −0.1 per cent (procedure I).

A similar, but simpler, procedure proposed by Raschig (*21*), in which the nitrite was added to permanganate, acidified, and let stand 2 minutes at room temperature before adding potassium iodide, yielded an average error of +0.1 per cent (procedure J). This procedure differs from that quoted by Laird and Simpson (*16*) as "Raschig's method" in that they have the nitrite and neutral permanganate stand together 2 minutes before acidifying, and not after, whereas Raschig (*21*) recommends acidifying and after 2 minutes adding potassium iodide. Kolthoff (*14*) used a similar procedure.

The procedure was also carried out as given by Laird and Simpson (*16*) with unsatisfactory results. Nitrite is not oxidized in neutral solution in the cold by potassium permanganate (*3*), and unless there is a short wait after acidifying, the oxidation of the nitrous acid may not be complete. Some of the solutions became blue again on standing after completion of the titration. Raschig (*21*) claims that in such a case the nitrous acid and the permanganate have not stood together long enough and all the nitrous acid has not been oxidized. It might be pointed out, however, that oxidation of hydriodic acid by the air will also cause the reappearance of the blue color.

Attempts to estimate nitrite by determining the amount of iodine liberated by it from potassium iodide, both in the air and in an atmosphere of carbon dioxide, according to the different procedures proposed by Davisson (*5*), Robin (*22*), Winkler (*26*), Raschig (iodide-nitrite reaction, *21*), and Clarke (*4*) proved unsatisfactory. Some of these require a technic which must be perfected by practice, and none is considered satisfactory from the standpoint of this investigation.

The methods proposed by Phelps (*20*) and Rupp and Lehmann (*23*) also failed to give satisfactory results.

Miscellaneous Methods

A method proposed by Sanin (*24*), using hydroxylamine hydrochloride which is titrated with standard sodium hydroxide before and after the reaction

$$NaNO_2 + NH_3O.HCl = NaCl + N_2O + 2H_2O$$

gave an average error of +0.4 per cent when using 50 mg. of sodium nitrite, but the average error with 100 mg. was −1.2 per cent.

The methods suggested by the publication of Grossman (*11*), Fischer and Steinbach (*7*), Moir (*18*), Grützner (*12*), and Green and Evershed (*9*) gave results with large and variable errors.

Summary

Thirty-one procedures were tried for the volumetric determination of nitrites. Ten proved satisfactory. Eight are listed as permanganate methods, and the other two, listed as iodometric methods, involve the oxidation of nitrite by acid permanganate.

Sanin's method with hydroxylamine hydrochloride proved satisfactory when not over 50 mg. of sodium nitrite were present.

When made with special precautions, potassium permanganate and sodium nitrite solutions were shown to be stable for some time.

It was shown that neither sodium oxalate nor ferrous ammonium sulfate solutions are stable for a period as long as one month. However, sodium oxalate is much more stable than ferrous ammonium sulfate.

Hydrogen peroxide, made up in 1.0 N sulfuric acid solution, was found to be stable for as long as 3 weeks.

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Determination of Carbon Dioxide in Continuous Gas Streams

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The problem of quantitative removal of carbon dioxide from continuous gas streams by absorption in barium hydroxide and its subsequent determination by direct titration has been investigated. An efficient absorber for carbon dioxide or other soluble gases, in which the absorbing solution may be directly titrated, is described.

The efficiency of absorption of soluble gases from a continuous gas stream is determined by the design of the absorption vessel, the concentration of the absorbing solution, and the rate of flow of the gas mixture. The efficiency of an absorption vessel is determined more by the length of the path of the gas bubbles through the absorbing liquid than by the extent of surface exposed to the gas stream.

The addition of barium chloride to barium hydroxide solution appreciably increases its efficiency in absorbing carbon dioxide from continuous gas streams. However, the small amounts generally used have but little practical effect. When solutions containing suspended barium carbonate are stirred with a current of carbon dioxide–free air they cannot be titrated with acid stronger than approximately 0.07 N.

In an attempt to study the effect of petroleum spray oils on the respiratory activity of growing plants, it was discovered that the carbon dioxide in the air drawn continuously from the respiration chambers could not be completely absorbed by the apparatus and methods generally used. As a foundation for subsequent work on respiration it was decided to investigate the methods for absorbing and quantitatively determining carbon dioxide in continuous gas streams.

For the benefit of those who are confronted with the problem of choosing, or devising, a method or determining carbon dioxide in other than routine studies, the results of a literature review are herein presented. The methods described in the literature have been developed largely in connection with the determination of carbon dioxide derived from the oxidation of organic substances in combustion analysis, from the oxidation of carbon in steel, from carbonates, and from the respiratory activities of living organisms. Upon the basis of differences in principle the methods may be briefly classified as follows:

1. Gravimetric Methods.
   a. Carbon dioxide absorbed in strong alkaline solutions, or solid absorbents, such as soda lime and ascarite (sodium hydroxide dispersed on asbestos fibers), and the increase in weight of absorbent determined.
   b. Absorbed in dilute solution of sodium or potassium hydroxide and weighed as barium carbonate.
   c. Absorbed in a strong solution of barium hydroxide and the resulting carbonate either weighed directly or converted to the corresponding sulfate.
2. Titrimetric Methods.
   a. Carbon dioxide absorbed in a dilute standard solution of sodium or potassium hydroxide and the carbonate determined by double titration, using phenolphthalein and methyl orange or other suitable indicators.
   b. Absorbed in a standard solution of barium hydroxide and the carbonate determined by a single titration.
   c. Absorbed in a dilute standard solution of sodium or potassium hydroxide, an excess of neutral barium chloride added, and the excess of alkali titrated.
   d. Absorbed in a strong solution of barium hydroxide and the resulting carbonate filtered, washed, dissolved in a standard acid solution, and titrated.
3. Gasometric Methods.
   a. By volumetric gas apparatus. Carbon dioxide absorbed directly in strong alkali in gasometric apparatus and the decrease in the volume of the gas mixture measured at atmospheric pressure; or absorbed in strong alkali, carbon dioxide liberated in an acid solution in a gas apparatus, and its volume measured at atmospheric pressure.
   b. By manometric gas apparatus. Carbon dioxide absorbed in strong alkali and liberated in the manometric gas

apparatus by excess acid. Volume of the gas then increased to a fixed value and its pressure measured manometrically.

4. Electrometric Methods.
   a. Electrolytic resistance method. Carbon dioxide absorbed in a standard solution of alkali, preferably barium hydroxide, and the decrease in its electrolytic conductivity measured.
   b. Thermal conductivity method. The concentration of carbon dioxide in a gas mixture is indicated by its thermal conductivity, which is determined by measuring the electrical resistance of a wire heated by a constant electric current and surrounded by the gases under study.
5. Colorimetric Method. Carbon dioxide absorbed in a solution of the sodium salt of phenolphthalein and its concentration indicated by color

Previous Investigations

The chief advantage of the gravimetric method is the relatively simple absorption apparatus which is permitted by the use of strong alkaline solutions or solid absorbents. The simplicity of the method is offset, however, by the precautions which are necessary in order to prevent moisture and other gases being collected in the absorption vessels. The disadvantages of the gravimetric methods have been discussed in detail by Cain (*6*) and Truog (*35*). Most of the objectionable features of the gravimetric methods have been overcome by Cain by absorbing the carbon dioxide in barium hydroxide and then weighing the barium carbonate, or its equivalent, as the corresponding sulfate.

Titrimetric methods are preferable to gravimetric methods in that they are more rapid and less tedious. Unlike the gravimetric methods, however, they necessitate the use of dilute standard alkaline solutions which absorb carbon dioxide less efficiently, and in consequence more elaborate absorption vessels must be employed. When dilute standard solutions of sodium and potassium hydroxides are used, the carbon dioxide absorbed is determined either by the double titration method of Brown and Escombe (*5*), or by precipitating the carbonate with neutral barium chloride and then determining the excess alkali by a single titration. The single titration method is simplified, however, by absorbing the carbon dioxide directly in a standard solution of barium hydroxide. Although some investigators, notably Humfeld (*19*), Willaman and Brown (*45*), Marsh (*24*), and Newton and Anderson (*27*), have obtained satisfactory results with the double titration method, the use of barium hydroxide with a single titration is more convenient. Various modifications of the single titration method have been described in the literature by Mack (*23*), Blackman and Parija (*4*), Neller (*26*), Tang (*34*), Schollenberger (*29*), Crozier and Navez (*10*), Heck, (*17*), and others.

The gasometric methods for determining carbon dioxide, especially those devised by Van Slyke (*36* to *41*) and his co-workers, Scholl and Davis (*28*), Blacet and Leighton (*3*), Chittick (*8*), and Coe (*9*), are capable of attaining a high degree of accuracy. They are designed, however, for determining the carbon dioxide in relatively small volumes of gases and therefore cannot be conveniently applied in the analysis of gas streams over extended periods.

The electrolytic resistance method was devised by Cain and Maxwell (*7*) for determining the carbon in steel and has been modified by Harvey and Regeumbal (*16*), Gane (*15*), and Ledebur (*21*). The necessity of expensive apparatus and careful temperature control has doubtless prevented this method from coming into general use. It is especially useful for determining progressively the respiration rate of living organisms, and for studying other reactions in which it is desired to measure the rate at which carbon dioxide is produced.

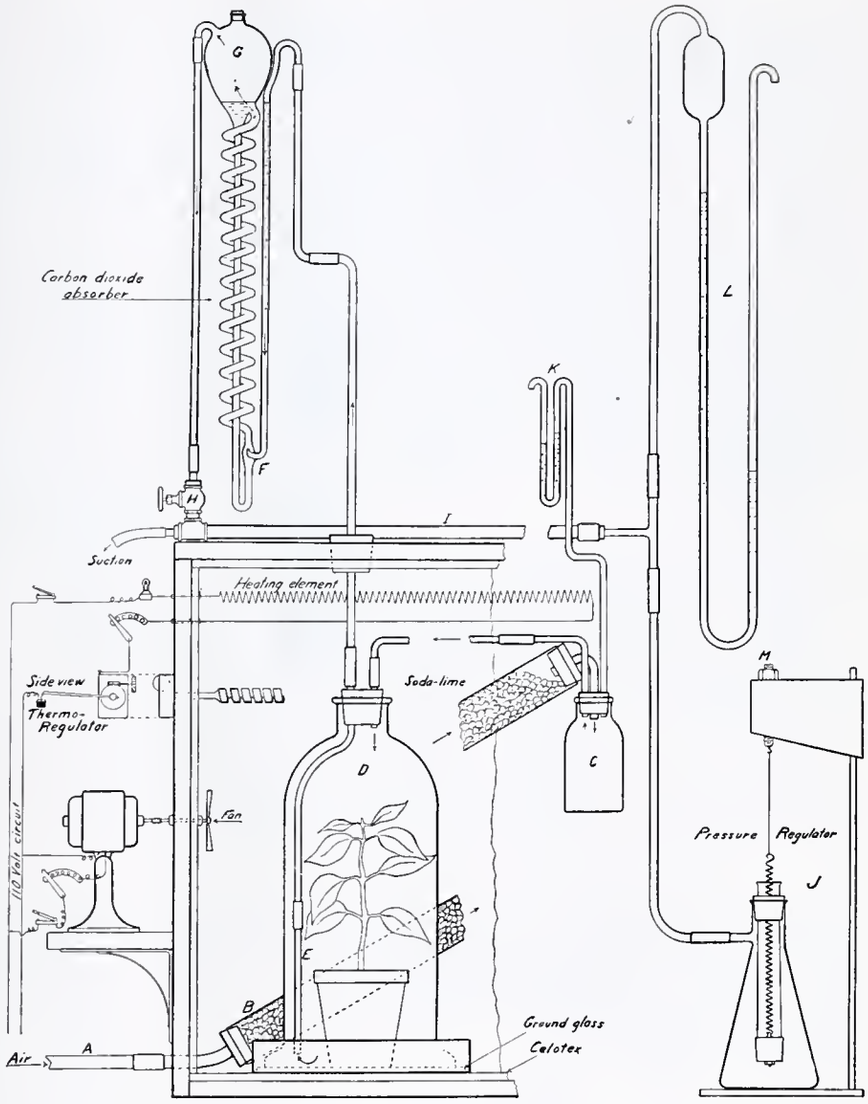

Figure 1. Constant Temperature Respiration Cabinet

The thermal conductivity method for determining the carbon dioxide in gas mixtures is based upon the principle that the thermal conductance of a gas is determined by its composition. The thermal conductivity of the gas may be determined by measuring the electrical resistance of a wire traversed by a constant electrical current and surrounded by the gas enclosed in a space, the walls of which are at a constant temperature. Precautions are, of course, taken to prevent the dissipation of heat energy from the wire by radiation, conduction through the ends of the wire, and by thermal convection. The theoretical aspects of the method have been discussed by Daynes (*12*, *13*), Shakespear (*31*, *32*), and by Weaver et al. (*44*). In the latter paper is presented an excellent review of the history of the development of the method, together with a valuable contribution in the way of experimental apparatus, methods, and data. Although the method has been used very largely for analysis of aliquots of gas mixtures, it has been applied satisfactorily in respiratory studies by Waller (*42*) and by Stiles and Leach (*33*).

A colorimetric method, based upon the relation of color to the amount of carbon dioxide absorbed by a solution of the sodium salt of phenolphthalein, has been described by Emmert (*14*) and Hughes (*18*). This method is apparently limited in its applications and has, therefore, not been used very generally.

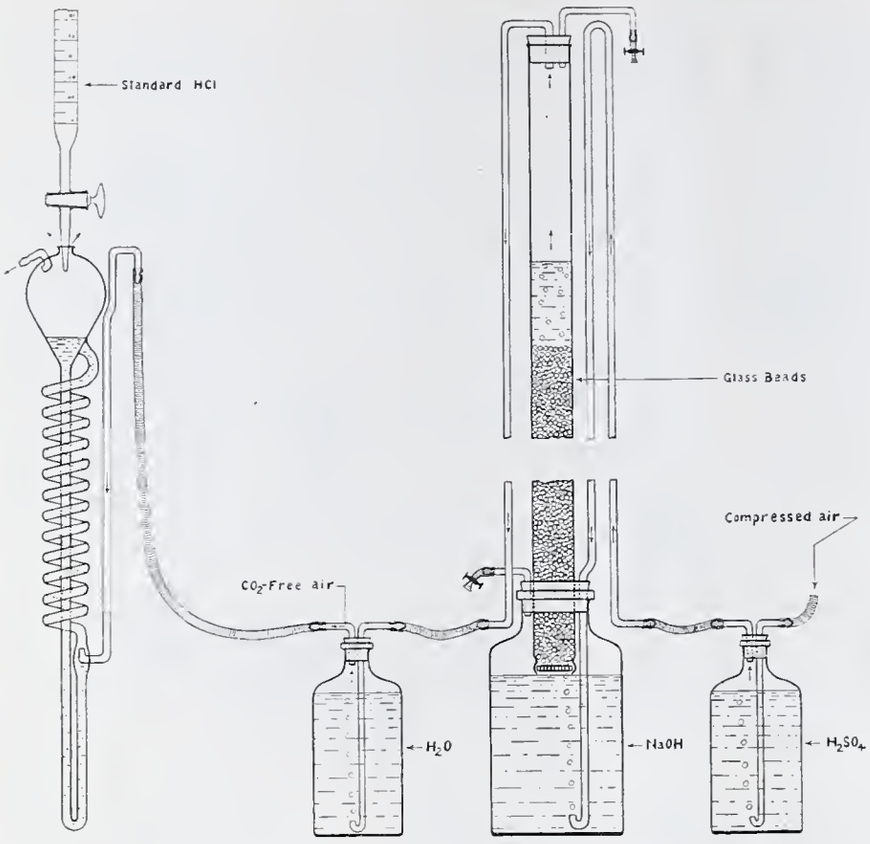

FIGURE 2. TITRATION APPARATUS

Under average laboratory conditions, the single titration method is, perhaps, the most satisfactory for determining carbon dioxide in continuous gas streams. It has therefore been applied in developing the methods and apparatus used in this investigation.

EXPERIMENTAL

APPARATUS AND METHODS. The respiration apparatus with accessories is shown in Figure 1. It consists of a constant temperature cabinet containing six respiration chambers with carbon dioxide absorbers, and is provided with a source of carbon dioxide-free air. The cabinet is constructed from wood, lined with Celotex, and is maintained at a constant temperature by a thermoregulator and an electric fan. The respiration chambers are formed by sealing glass bell jars to ground-glass plates with a compound prepared by melting together 16 parts of vaseline, 4 parts of raw rubber, and 1 part of paraffin. As a precaution against leakage the chambers are set in shallow trays of water. A stream of carbon dioxide-free air is supplied by drawing air from outside the laboratory through a large soda-lime tube, 5 cm. in diameter and 62 cm. long, placed inside the cabinet in order to bring the temperature of the incoming air to that of the cabinet.

The material to be studied is placed in chamber *D*. Air is drawn from outside the laboratory by suction, entering the cabinet through tube *A*, and passing slowly upward to *C* through the soda-lime tube *B*. From the latter it is distributed to each of the six respiration chambers, only one of which is shown at *D* in the diagram. The carbon dioxide-free air enters the top of the chamber, carrying downward with it the carbon dioxide respired by the plant or other material being studied. The carbon dioxide-laden air is drawn from the bottom of the chamber through tube *E* and is discharged from the jet *F* into absorber *G*, which is charged with barium hydroxide solution. The rate at which the gas mixture passes through each absorber is adjusted by the needle valve *H*, the rate being determined by calibrating with a liquid displacement method. The needle valves are not altered after calibration.

The suction applied to the system is maintained constant by the pressure regulator *J*, which consists of a valve formed by a rubber stopper seated against the end of a 25-mm. glass tube. The end of the tube is ground to form a tight joint, and the valve (stopper) is held in place by a spiral spring, the tension of which is adjusted by the nut *M*. The reduced pressure (suction) of the system is indicated by the water manometer *L*, and the pressure inside the respiration chambers is indicated by the manometer *K*.

When all six respiration units are in operation with the gas mixture passing through each at the rate of 20 liters per hour, the pressure in the chambers is not reduced by more than 1 cm. of water below that of the atmosphere.

In making the determinations, ample time is allowed for the temperature of the material in the respiration chambers to come to equilibrium. Atmospheric carbon dioxide remaining in the apparatus after being assembled is removed by aspirating with carbon dioxide-free air for 2 hours before connecting with the absorption vessel. At the end of the respiration period the absorption vessels are removed and connected with the apparatus in Figure 2, and the excess barium hydroxide titrated against 0.0454 *N* hydrochloric acid (1 ml. equals 1 mg. of carbon dioxide), using phenolphthalein or thymolphthalein as an indicator. The carbon dioxide-free compressed air supplied by the above apparatus not only stirs and circulates the liquid in the absorption vessel during titration, but it also prevents the diffusion of atmospheric carbon dioxide into the apparatus. Although phenolphthalein is most generally used as an indicator, it is not entirely satisfactory on account of the indefiniteness of its end point. Its transition range is from pH 8.3 to 10.0 and consequently it shows a faint color due to the slight solubility of the suspended barium carbonate. Schollenberger (*30*) has recommended thymolphthalein as a more satisfactory indicator for the titrimetric estimation of carbon dioxide. It shows a sharper end point because its transition range is narrower and above the region of reaction of the dissolved barium carbonate. Obviously, the same indicator must be used in making the blank titration.

Of the various gas absorption vessels described in the literature, those designed by Weaver and Edwards (*43*), Milligan (*25*), Beaumont, Willaman, and DeLong (*1*), and Harvey and Regeumbal (*16*) are probably the most efficient. The absorbers described by Beaumont, Willaman, and DeLong and by Milligan are the only ones designed to permit titration directly in the vessel. Milligan absorbers, having been used in a previous investigation, were available, and were therefore used in the present experiments. A serious objection to these absorbers, however, is their large capacities for the absorbing liquid. They will not operate properly with a volume of less than 130 ml. of liquid, and, consequently, relatively weak alkali solutions have to be used in order not to exceed the capacity of the vessels in titrating with dilute standard acid. Strong acids cannot be used in titrating in the presence of suspended barium carbonate.

In a preliminary investigation the respiration rates of standard bean seedlings were determined, using Milligan absorbers with the respiration cabinet shown in Figure 1. The absorbers were charged with 60 ml. of 0.0454 *N* barium hydroxide and 70 ml. of distilled water neutralized with barium hydroxide, using phenolphthalein as an indicator.

The absorptions extended over 2-hour periods and the titrations were made with 0.0454 N hydrochloric acid, as already described.

An analysis of the data obtained in these experiments indicated that the carbon dioxide was not being completely absorbed. Consequently, the Milligan absorbers were abandoned and some time devoted to the development of apparatus better suited to the problem undertaken.

The bead absorber shown in Figure 3 was first developed, but was found to be unsatisfactory in that it necessitated the use of not less than 60 ml. of absorbing liquid. Barium hydroxide solutions stronger than 0.105 N could not be used in these absorbers on account of the excessive volume of standard acid required in titration.

The spiral absorber shown in each of the three figures was finally developed and was found to be highly satisfactory. It will operate efficiently on 30 ml. of absorbing liquid, thus permitting relatively concentrated solutions of barium hydroxide to be titrated without using excessive volumes of standard acid. The spiral is 40 mm. in diameter and is made from 4-mm. (inside bore) tubing. The reservoir has a capacity of 200 ml.

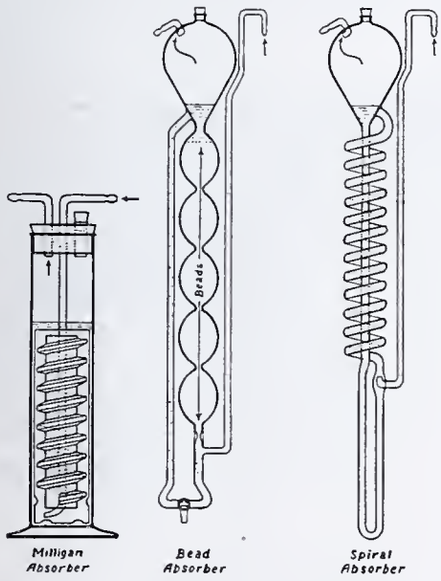

Figure 3. Absorption Vessels

Efficiency of Absorbers. The efficiency of each of the absorbers was determined by passing through it a current of air at the rate of 20 liters per hour, into which was liberated a known amount (29.1 mg.) of carbon dioxide. This was accomplished by slowly dropping 50 ml. of 0.0264 N sodium carbonate solution into 100 ml. of 1.0 N sulfuric acid. The sodium carbonate solution was run into the sulfuric acid in a closed flask from a pipet, the orifice of which was adjusted to deliver 50 ml. in 20 minutes. A current of carbon dioxide–free air was bubbled through the sulfuric acid solution carrying the carbon dioxide liberated to the absorber. The stream of carbon dioxide–free air was passed through the system for 40 minutes after adding the sodium carbonate solution in order to sweep into the absorber any carbon dioxide remaining in the system. Three absorbers were inserted in the chain so that the carbon dioxide not absorbed in the first would be caught in the other two.

The efficiency of absorption, as influenced by the concentration of barium hydroxide in the absorbing liquid, was determined for each of the three absorbers. Concentrations of barium hydroxide greater than 0.0525 and 0.105 N could not be used with the Milligan and bead absorbers, respectively, on account of the large volumes of standard acid required in titration. An attempt was made to titrate the large volumes of standard barium hydroxide solutions in these absorbers by first adding a measured volume of strong standard acid and then titrating to the end point with weak acid. However, these studies showed that when the strong acid was added in the presence of suspended barium carbonate, carbon dioxide was liberated by local concentrations of the acid. The carbon dioxide was lost by being aspirated from the solution by the carbon dioxide–free air used to stir and circulate the liquid in the absorber during titration. With this method it was shown that acid more concentrated than approximately 0.07 N could not be used in titrating barium hydroxide solutions containing suspended barium carbonate without losing carbon dioxide. The effect of rate of flow of the gas mixture on the efficiency of absorption, using 0.0167 N and 0.105 N barium hydroxide, was also investigated. The results of these studies are presented in Tables I and II.

Table I. Comparative Efficiencies of Spiral, Bead, and Milligan Absorbers

(Gas mixture passed through absorber at 20 liters per hour. 29.1 mg. carbon dioxide present)

Absorbing Liquid $Ba(OH)_2$	Spiral Absorber CO_2 absorbed	Spiral Absorber Efficiency	Bead Absorber CO_2 absorbed	Bead Absorber Efficiency	Milligan Absorber CO_2 absorbed	Milligan Absorber Efficiency
	Mg.	%	*Mg.*	%	*Mg.*	%
0.1050 N	29.2	100.1	27.6	95.1	....	....
0.0780 N	29.1	100.0	27.3	94.7	....	....
0.0525 N	28.6	98.6	25.7	88.6	27.7	95.5
0.0350 N	28.6	98.6	24.3	83.8	26.1	89.8
0.0262 N	27.9	96.2	23.9	82.5	25.9	89.3
0.0210 N	27.4	93.8	23.7	81.8	25.9	89.3
0.0175 N	25.7	88.6	23.0	79.4	24.1	83.2

Table II. Efficiency of Spiral Absorber with Gas Mixture Flowing at Different Rates

(Absorber charged with 0.067 N and 0.105 N $Ba(OH)_2$)

Rate of Flow of Gas Mixture	Carbon Dioxide Absorbed 0.067 N $Ba(OH)_2$	Carbon Dioxide Absorbed 0.105 N $Ba(OH)_2$	Efficiency 0.067 N $Ba(OH)_2$	Efficiency 0.105 N $Ba(OH)_2$
Liters/hr.	*Mg.*	*Mg.*	%	%
20	29.2	29.2	100.1	100.1
25	28.4	28.1	97.8	97.0
30	28.2	27.7	97.2	96.6
40	25.6	26.2	88.3	90.3
50	22.1	24.9	76.3	85.8

Effect of Barium Chloride on the Efficiency of Absorption of Carbon Dioxide by Barium Hydroxide Solutions. A number of investigators recommend the addition of barium chloride to the barium hydroxide solution. As observed by Mack (*23*), the mass-action effect of barium chloride reduces the solubility and hydrolysis of the barium carbonate. In the present work this would not only increase the efficiency of absorption of carbon dioxide, but would tend to prevent the decomposition of barium carbonate by local concentration of the acid added in titration.

Table III. Efficiency of Absorption of Carbon Dioxide by 0.0175 N Barium Hydroxide in Spiral Absorber, as Influenced by Different Concentrations of Barium Chloride

Concentration of $BaCl_2$	Carbon Dioxide Absorbed Absorber 1	Absorber 2	Absorber 3	CO_2 Recovered in First Absorber Efficiency
	Mg.	*Mg.*	*Mg.*	%
0.00 N	26.4	3.3	0.0	89.5
0.01 N	26.5	3.3	0.0	89.8
0.10 N	27.0	2.6	0.0	91.5
0.20 N	27.5	2.3	0.3	93.2
0.40 N	27.7	2.4	0.2	93.9
0.80 N	28.0	1.8	0.0	94.8

A series of determinations were, accordingly, carried out, using various concentrations of barium chloride. To show the influence of the latter more effectively, a very dilute solution (0.0175 N) of barium hydroxide was used. The concentrations of barium hydroxide and barium chloride

in the solutions were adjusted by adding measured amounts of 1.0 N barium chloride and conductivity water to a measured volume of 0.105 N barium hydroxide. The results of these studies are presented in Table III.

Discussion

The data show clearly that the efficiency of absorption of carbon dioxide from a continuous gas stream is determined by the concentration of the absorbing liquid, by the rate of flow of the gases, and by the design of the absorption apparatus. Although it is generally assumed that a bead column is highly efficient in absorption, on account of the large surface of the absorbent exposed to the gases, these studies show it to be less efficient than either the spiral or Milligan absorbers. The average of the values for the efficiency of absorption for the five concentrations of barium hydroxide, ranging from 0.0175 N to 0.0525 N, is 83.22, 89.42, and 95.16 per cent for the bead, the Milligan, and the spiral absorber, respectively. These differences are apparently due to the differences in the length of the path of the gas through the three vessels. The gas bubbles travel approximately 39 cm. in the bead, 76 cm. in the Milligan, and 142 cm. in the spiral absorber. The higher efficiency of the spiral and the Milligan absorbers may also be attributed to the stirring action of the walls of the tubes as the alternate columns of liquid and gas pass upward through them. As indicated by the work of Ledig and Weaver (*22*) and by Davis and Crandall (*11*), the layer of liquid at the gas-liquid interface reaches equilibrium with the gas very quickly, and unless the dissolved gas is carried into the interior of the liquid by convection, the rate of absorption of the gas is determined by its diffusion rate in the liquid. The surface or stationary film is, of course, not stirred by the movement of the bubble through the tube, but the liquid adjacent to it is continuously renewed, thus removing the dissolved gas into the interior of the column of liquid following each gas bubble.

The method of titrating directly in the absorption vessel in the presence of suspended barium carbonate raises the question as to whether or not carbon dioxide is lost through the decomposition of the carbonate by the acid added during the titration. Truog (*35*), Bergman (*2*), Mack (*23*), and others have investigated this problem by the conventional method of shaking the solution during titration, and have concluded that the barium carbonate in the barium hydroxide solution does not affect the results. In this investigation, however, the solutions were stirred and circulated in the absorption vessels during titration by a current of carbon dioxide-free air, which would obviously remove by aspiration any carbon dioxide formed by local concentrations of acid. A series of titrations was, therefore, made with standard acid of various concentrations. The effect of adding the acid at different rates was also studied. These studies showed that when solutions containing suspended barium carbonate are stirred with a current of carbon dioxide-free air during titration, carbon dioxide is lost if titrated with a standard acid stronger than approximately 0.07 N.

As shown by the data in Table III, the addition of barium chloride to 0.0175 N barium hydroxide solution increased quite markedly its efficiency in absorbing carbon dioxide. It may be noted, however, that an equivalent weight or more of barium chloride per liter of barium hydroxide solution must be used in order to be of any practical value; and that the small amounts generally used have but slight effect. Kostychev (*20*), for example, recommends the addition of 1 gram, or 0.0096 equivalent weight of barium chloride to each liter of barium hydroxide solution. Mack (*23*) used 4.5 grams, or 0.0432 equivalent weight per liter. Obviously the mass action of such low concentrations could have but slight practical effect; and this was quite apparent in these studies. The effect would be even less with the more concentrated barium hydroxide solutions which are generally used.

According to Mack (*23*) the barium chloride reduces the solution and hydrolysis of the barium carbonate during titration. In this work, however, the standard acid used in titrating the barium hydroxide solution was so dilute (0.0454 N) that no carbon dioxide was liberated from the suspended barium carbonate by local concentrations of the acid. The increase in the carbon dioxide recovered must, therefore, have been due to the mass-action effect of the barium chloride in increasing the absorption of carbon dioxide by the barium hydroxide solution, and not to its effect in reducing the loss of carbon dioxide during titration.

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Apparatus and Methods for Precise Fractional-Distillation Analysis[1]

II. Laboratory Columns for Precise and Rapid Fractionation of Gaseous and Liquid Samples

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This paper reports the findings of intensive theoretical and experimental study of precise low- and high-temperature laboratory fractionating columns under the headings of the following factors which are shown to be of fundamental importance as well as highly convenient for direct experimental determination or control:

Composition and distilling characteristics of sample.

Total time of distillation.

Regulation of distillation rate, reflux ratio, distillation pressure, and all other variables except total time of distillation.

Ratio of 10 times the hold-up of material in the fractionating section (excluding reflux or condenser) to maximum column capacity.

Ratio of 10 times the hold-up of material in reflux condenser section to maximum column capacity.

Effectiveness of column packing in securing repeated and intimate contact of refluxed liquid and ascending vapor.

Efficiency of thermal insulation of column.

General design and construction of fractionating columns and apparatus.

Fractionating columns are described having an entirely separate sleeve-like metal reflector type vacuum jacket for thermal insulation at all temperatures ranging from −190° C. up to 300° C., within which jacket any of a large variety of distilling tubes of various diameters may be inserted for the rapid and precise fractionation of gaseous or liquid samples ranging from a fraction of a liquid cubic centimeter to as much as 20,000 cc. These distilling tubes are packed with highly effective, spiral, continuous, uniform, wire-coil packings shown to be superior to the usual chance-arrangement noncontinuous column packings. Complete distillations with the apparatus assembly described take from one hour to several hours' time, depending on the requirements; and the separation accomplished in a single distillation is materially superior to that possible with previously described laboratory fractionating columns including even extremely tall experimental columns operated at exceedingly slow rates.

THIS article presents the results and conclusions of exhaustive theoretical and experimental investigations and seven years' experience in the development and intensive use of laboratory columns of high-fractionating effectiveness suitable for distilling components with boiling points ranging from −190° C. to 500° C. This extreme range comprises practically all components which would be considered distillable, except a few gases like helium and carbon monoxide, noncondensable in liquid air, and the very high-boiling petroleum and coal-tar pitches, asphalts, etc.

In the course of this work, all available results of previous and contemporary investigators of laboratory fractionating columns and apparatus were carefully reviewed and in many cases experimentally investigated. The literature on laboratory fractionating columns is exceedingly voluminous and has already been reviewed by Young (*26*), Leslie (*17*), Hill (*16*), and others.

FUNDAMENTALS OF DESIGN AND RATINGS OF COLUMNS

In many ways the fractionating columns described in this and a previous paper (*19*) differ radically from other laboratory fractionating columns previously described. In making comparisons of efficiency, the question of the fundamentals of design and quantitative comparison of laboratory batch columns to be used for precise analytical work naturally presents itself. The problem is highly complicated, including such variables as amount of sample taken, total time of distillation, method of varying rate of distillation, efficiency of column insulation, column and accessory apparatus design, etc. Previous investigators (*7, 16, 18, 26*) are not in agreement on the correct method of comparing and rating columns, as is evident from the discrepancies in their conclusions as to the merits of the same column designs.

It is assumed in this paper that the user of a precise fractionating column is primarily interested in the most accurate possible analytical determination of a more or less complex sample in least total time for the distillation. The size of the sample distilled will be an important but usually a secondary consideration. In some cases, it will be desired to separate largest possible quantities of pure or substantially pure compounds or very close-cut fractions in reasonable time. However, the second requirement is not necessarily opposed to the first, and confusion will be avoided by considering only the first requirement.

The analytical fractionating column is of necessity a batch distillation column as opposed to continuous distillation apparatus. The logical way of expressing the results of an analytical batch distillation is in the form of a plot of the overhead temperatures or some other physical property such as density, refractive index, etc., and the corresponding total collected distillate expressed in per cent of the original sample, or the so-called "fractional distillation curve." If we

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The original features of the apparatus described in this article are covered by foreign patents and United States and foreign pending patent applications and are manufactured and distributed exclusively by the inventor.

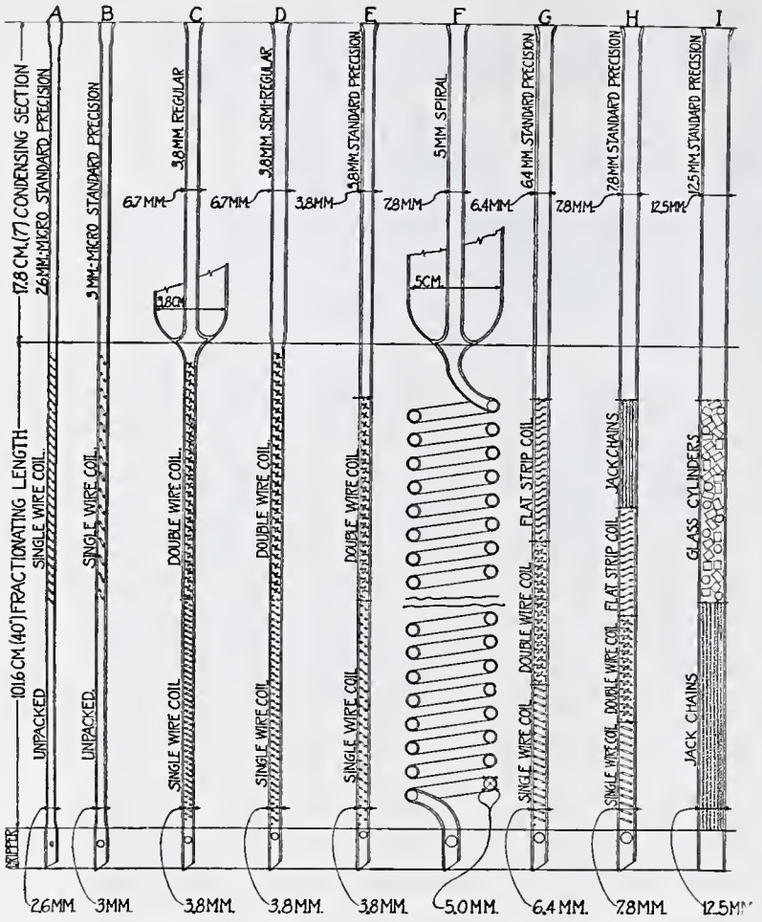

FIGURE 1. DISTILLING TUBES AND PACKINGS USED IN EXPERIMENTS

A. Single-wire coil, 7.9 turns per inch (3.12 turns per cm.), No. 26 (0.037 cm. diameter) monel wire
B. Single-wire coil, 5.2 turns per inch (2.05 turns per cm.), No. 26 monel wire
C. Single-wire coil, 7 turns per inch (2.76 turns per cm.), No. 20 (0.0812 cm. diameter) monel wire
Double-wire coil: Outer coil, 7 turns per inch (2.76 turns per cm.), No. 20 monel wire. Inner coil, 4 turns per inch (1.57 turns per cm.), No. 20 monel wire
D. Single-wire coil, 7 turns per inch (2.76 turns per cm.), No. 20 monel wire
Double-wire coil: Outer coil, 7 turns per inch, No. 20 monel wire. Inner coil, 4 turns per inch, No. 20 monel wire
E. Single-wire coil, 7 turns per inch, No. 20 monel wire
Double-wire coil: Outer coil, 7 turns per inch, No. 20 monel wire. Inner coil, 4 turns per inch, No. 20 monel wire
F. 38 turns, approximately 43 mm. outside diameter of 5.0 mm. inside diameter Pyrex standard tubing (unpacked); total vertical length of coiled portion 50.8 cm. (20 inches); uncoiled, 400 cm.
G. Single-wire coil, 5.5 turns per inch (2.16 turns per cm.), No. 18 (0.1024 cm. diameter) monel wire
Double-wire coil: Outer coil, 5.5 turns per inch (2.16 turns per cm.), No. 18 monel wire. Inner coil, 4.5 turns per inch (1.77 turns per cm.), No. 18 monel wire
Flat-strip coil, 6 turns per inch (2.36 turns per cm.) of copper strip about 0.21 cm. × 0.09 cm. in cross section
H. Single-wire coil, 4.5 turns per inch (2.16 turns per cm.), No. 18 monel wire
Double-wire coil: Outer coil, 4.5 turns per inch, No. 18 monel wire. Inner coil, 3.5 turns per inch (1.38 turns per cm.), No. 18 monel wire
Flat-strip coil, 6 turns per inch (2.36 turns per cm.) of copper strip about 0.21 cm. × 0.1 cm. in cross section
Jack chains, 8 strands, No. 22 brass single jack chains
I Jack chains, 23 strands, No. 22 brass single jack chains
Glass cylinders, 5 mm. outside diameter × 5 mm. long glass cylinders, walls about 1.2 mm. thick

assume that the separation obtained is sharp enough to result in perfectly horizontal plateaus for the pure components (or constant-boiling mixtures) in the sample, separated by more or less sloping breaks, then the amount of the intermediate mixed fraction indicated by the curve is a very definite and very useful criterion of the performance of the column. The smaller the intermediate fraction (approaching the value of zero for the ideal staircase break), the more accurate the analysis. For difficult separations or for inefficient columns, the break will be less sharply defined; however, the concept of the intermediate fraction as a criterion of analytical accuracy is of general usefulness.

The investigation of the mechanism of fractional distillation by theoretical reasoning alone, while obviously most desirable, is insufficient without recourse to extensive experimentation, especially when development of actual equipment and methods is the object. The author has therefore found it expedient to express arbitrarily all the important variables which affect the size of the intermediate fraction per cent as eight factors, each subject to exact measurement and to greater or lesser control. These factors are not necessarily independent of each other and the form of the connecting functions may be obscure. The only justification for setting them up is to facilitate the exact experimental study of changes in column design and operation.

The size of intermediate fraction per cent is a function of and is completely determined by the following factors:

1. Composition and distilling characteristics of sample and of the vapor entering the column.
2. Total time of distillation.
3. Regulation of (*a*) distillation rate, (*b*) reflux ratio, (*c*) distillation pressure, and (*d*) all other operating variables except total time of distillation.
4. Ratio of 10 times the hold-up of material in the fractionating section (excluding reflux or condenser) to maximum column capacity.
5. Ratio of 10 times the hold-up of material in reflux or condenser section to maximum column capacity.
6. Scrubbing effectiveness of column packing.
7. Efficiency of thermal insulation of column.
8. General design and construction of fractionating column and apparatus.

All these factors have been investigated experimentally, usually by actual intensive use of a large variety of apparatus modifications supplemented by fundamental research on the more important factors.

FACTOR 1. COMPOSITION AND DISTILLING CHARACTERISTICS OF SAMPLE AND OF VAPOR ENTERING COLUMN

The following general observations are made on the basis of a great number of low- and high-temperature distillations of a variety of commercially important as well as synthetic mixtures. The observations are in substantial agreement with previous literature on this subject.

For ideal solutions it can be shown that the amount of the intermediate fraction is approximately inversely proportional to the difference in boiling points of the two components separated. However, highly complex mixtures are more difficult to separate than less complex mixtures, even though the components to be separated are present in the same percentage and the differences in boiling points of these components from the other components adjacent on the fractional distillation curve are the same for both cases. This fact should be kept in mind in testing columns with synthetic mixtures of only a few compounds as against distillation of commercial solvents, petroleum products, or other exceedingly complex products.

The lower the average molecular weight of a mixture, the more amenable it is likely to be to separation by fractional distillation. For instance, natural gas and in general all gaseous mixtures consist of comparatively few components with large differences in boiling point. Practically any normally gaseous mixture can be completely analyzed into its individual components by a combination of precise low-temperature fractionation and supplementary tests as previously discussed (*20*, *23*, *27*). With increasing molecular weight, the difference in boiling point between successive normal hydrocarbons decreases, and the number of isomers present increases considerably. This is shown clearly in the graphical presentation of boiling points of typical hydrocarbons and other compounds and in the illustrative fractional distillation curves in Part III of this series.

The composition of petroleum has long been a fascinating mystery, except in the case of the lower-boiling hydrocarbons up to about decane. With the aid of the apparatus described

in this and succeeding papers, it is possible to distil petroleum products fractionally and obtain very well defined and consistently recurring plateaus. These plateaus may be pure hydrocarbons, mixtures of hydrocarbons of almost identical boiling point, or constant-boiling mixtures. Many of the breaks between plateaus are poorly defined and seem to show poor separation. In every case, when such apparently poor breaks were investigated by extremely careful refractionation, intermediate plateaus of components (or constant-boiling fractions) occurring in small percentages were discovered.

Factor 2. Total Time of Distillation

Given a particular apparatus, there will be a certain optimum total time of distillation, below which the accuracy of separation suffers unduly and above which the increased sharpness of separation does not justify the extra time. The more effective the fractionating column, the shorter will be the total time of distillation to secure the desired results. The amount of hold-up of material in the reflux or condensing section of the column is frequently a controlling factor as to time of distillation and the time of distillation may be increased several times, by the use of large-diameter condensing tubes with bulky seals or with reflux partitioning devices, over the time which would be required with a column designed for least practical hold-up in the reflux. With the apparatus described in this series of papers, the time of distillation varies from as little as 1.5 hours to 5 or more hours (averaging 3 to 4 hours for most routine determinations), depending entirely on the nature of the sample and on the requirements of the analysis, but including a range of sample size from one to several thousand cubic centimeters and for either low- or high-temperature distillations. Typical results showing extremely sharp fractionation are given in Figures 4 to 13 of Part III of this series, which show far sharper separation than the results of similar distillations in columns several stories high (*5*, *14*) and taking as many as five days. It will be shown in this paper that even infinite time cannot compensate for poor rating in factors 4, 5, 6, and 7.

Factor 3. Regulation of Distillation Rate, Reflux Ratio, Distillation Pressure, and Other Operating Variables

The following variables comprise the procedure of fractional distillation analysis. The same column and apparatus will give widely different results according to the procedure used. The following generally valid observations are made, keeping in mind the fundamental criterion of least size intermediate fractions per time of complete distillation.

(*a*) The amount of vapor entering the bottom of the column is of course proportional to the heat supplied to the still. Contrary to most accepted practice, it has been found in the present investigation that best fractionation can be obtained by regulating the heat to still and reflux cooling so that the packing of the column is barely wet (*24*). The reasons for this will be evident from the discussion under factors 4 and 5.

(*b*) Reflux ratio should be varied according to difficulty of fractionation rather than maintained constant. More specifically, the reflux ratio should be inversely proportional to the tangent of the fractional distillation curve; as in the case of the automatic recording and control mechanism for low-temperature fractionation analysis described in Part IV[2] of this series. This procedure is far more economical of time and yields better fractionation than maintaining the reflux ratio constant or following any other procedure.

(*c*) Distillation pressure is preferably maintained constant at atmospheric. When the upper limit of the reflux temperature is reached or when the still temperature approaches the temperature of incipient thermal decomposition of sample, it becomes necessary to lower distillation pressure. This should be done abruptly in steps, in order to be able to control the distillation properly, and to facilitate the recording and correction for pressure of the temperature readings. The second distillation pressure may conveniently be about 40 mm., and the third pressure 5 mm. or lower. For distillation pressures lower than about 1 mm., packed fractional distillation columns are not suitable because of excessive pressure drop and for other reasons (*24*).

(*d*) For precise fractionation it is essential to have precise and practically lagless control of heat supply to still, reflux cooling, distillation pressure, etc. Otherwise it will neither be possible to adjust the reflux ratio in the manner described above nor to maintain the column precisely at the desired condition of wetness of packing.

All these operational variables appear complicated and difficult to standardize and record. However, in practice, it has been found possible so to standardize on manual operation that different operators will secure very similar results in practically the same total distillation time. It has also been found possible to develop an automatic recording and control mechanism, adapted for low-temperature fractionation analysis, in which practically all the important operational variables as included under factor 3 are fixed by a few simple adjustments of the apparatus.

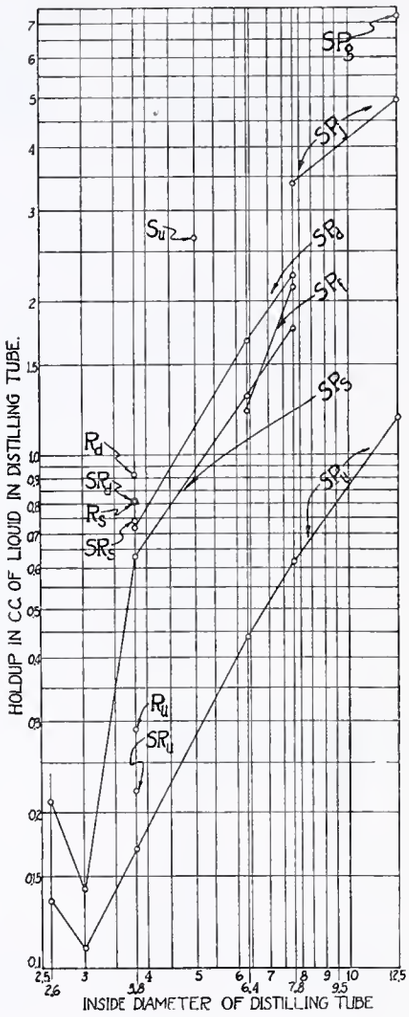

Figure 2. Experimentally Determined Total Hold-Up of Liquid in Various Distilling Tube and Packing Combinations

SP, Standard Precision distilling tubes, labeled *A*, *B*, *E*, *G*, *H*, and *I* in Figure 1
R, Regular distilling tube, labeled *C* in Figure 1
SR, Semi-Regular distilling tube, labeled *D* in Figure 1
S, spiral distilling tube, labeled *F* in Figure 1
Subscripts: *u*, unpacked. *s*, single-wire coil. *d*, double-wire coil. *f*, flat-strip coil. *j*, jack chains. *g*, glass cylinders

Factors 4 and 5. Ratio of Ten Times Hold-Up of Material in Fractionating and Condensing Sections to Maximum Column Capacity

Factors 4 and 5 are evaluated on the basis of the same set of experimental data. Otherwise, they are entirely distinct and independent, and two columns may have the same rating of the one factor and differ several hundred per cent on the rating of the other. Both factors, especially factor 5, have been found to be of great importance in their effect on the amount of the intermediate fraction per cent. Accordingly, a complete experimental study was made of a variety of distilling tube and packing combinations to determine their ratings for factors 4 and 5.

Description of Distilling Tubes. Figure 1 illustrates and gives all dimensions and details of nine distilling tubes of varying diameter in combination with several different types

[2] Part IV is to be printed in the Analytical Edition of May 15, 1933.

Table I. Experimental and Computed Data on Hold-Up, Maximum Distilling Capacity, and Factors 4 and 5 Ratings on Various Distilling Tubes and Packings (See Figure 1)

Description of Distilling Tube	Characteristic Properties[1]	No Packing	Single-Wire Coil Packing	Double-Wire Coil Packing	Helical Flat-Strip Packing	Jack Chain Packing	Glass Cylinder Packing
A Standard Precision micro-distilling tube 2.6 mm. inside diameter	*a*[2]	0.133	0.21	...	..	...	..
	b	0.028	0.028	...	..	...	..
	c	0.0000	0.002	...	..	...	..
	d	0.161	0.236	...	..	...	..
	e	0.020	0.020	...	..	...	..
	f	0.0045	0.0045	...	..	...	..
	g	0.0245	0.0245	...	..	...	..
	h	0.1365	0.2115	...	..	...	..
	i	Zero	2.75	...	..	...	..
	j	∞	0.77	...	..	...	..
	k	∞	0.089	...	..	....	..
B. Standard Precision micro-distilling tube 3.0 mm. inside diameter	*a*	0.11	0.14	...	..	...	..
	b	0.038	0.038	...	..	...	..
	c	0.00	0.002	...	..	...	..
	d	0.148	0.176	...	..	...	..
	e	0.016	0.016	...	..	...	..
	f	0.006	0.006	...	..	...	..
	g	0.022	0.022	...	..	...	..
	h	0.126	0.154	...	..	...	..
	i	3.5	4.0	...	..	...	..
	j	0.359	0.385	...	..	...	..
	k	0.0629	0.055	...	..	...	..
C. Regular distilling tube 3.8 mm. inside diameter	*a*	0.29	0.81	0.91	..	...	..
	b	0.081	0.081	0.081	.	...	..
	c	0.000	0.006	0.0091	..	...	..
	d	0.371	0.885	0.982	..	...	..
	e	0.120	0.120	0.120	..	...	..
	f	0.030	0.030	0.030	..	...	..
	g	0.176	0.176	0.176	..	...	..
	h	0.196	0.710	0.806	..	...	..
	i	7.01	4.36	3.14	..	...	..
	j	0.279	1.63	2.57	..	...	..
	k	0.250	0.403	0.559	..	...	..
D. Semi-Regular distilling tube 3.8 mm. inside diameter	*a*	0.22	0.74	0.81	..	...	..
	b	0.079	0.079	0.079	..	...	..
	c	0.00	0.006	0.009	..	...	..
	d	0.299	0.813	0.880	..	...	..
	e	0.075	0.075	0.075	..	...	..
	f	0.028	0.028	0.028	..	...	..
	g	0.103	0.103	0.103	..	...	..
	h	0.196	0.710	0.777	..	...	..
	i	7.01	4.36	3.14	..	...	..
	j	0.279	1.63	2.47	..	...	..
	k	0.147	0.237	0.328	..	...	..
E. Standard Precision distilling tube 3.8 mm. inside diameter	*a*	0.17	0.63	0.72	..	...	..
	b	0.06	0.06	0.06	..	...	..
	c	0.00	0.006	0.009	..	...	..
	d	0.23	0.684	0.771	..	...	..
	e	0.025	0.025	0.025	..	...	..
	f	0.009	0.009	0.009	..	...	..
	g	0.0344	0.034	0.034	..	...	..
	h	0.196	0.649	0.736	..	...	..
	i	7.01	4.36	3.14	..	...	..
	j	0.279	1.49	0.0234	..	...	..
	k	0.015	0.0788	0.109	..	...	..

[1] *a* and *i* experimentally determined, others derived or computed.

[2] *a*, Total hold-up of liquid in distilling tube
b, Total hold-up of vapor in distilling tube
c, Correction for packing volume, to be subtracted from *b*
d, Total liquid and vapor hold-up in distilling tube, obtained by subtracting *c* from the sum of *a* and *b*
e, Hold-up of liquid in condensing section
f, Hold-up of vapor in condensing section
g, Total liquid and vapor hold-up in condensing section, obtained by adding *e* to *f*
h, Hold-up of liquid and vapor in fractionating section only, obtained by subtracting *g* from *d*
i, Maximum distilling capacity of distilling tube
j, Factor 4 rating, obtained by dividing *h* by *i*
k, Factor 5 rating, obtained by dividing *g* by *i*

of packings as shown. These distilling tube elements may of course be combined with any desired type of lagging, still heating and reflux cooling parts, etc., to make up a complete column assembly. They may be used as parts of complete vacuum-jacketed fractionating assemblies, such as those shown in Figures 16 and 17. It will be shown that a highly efficient vacuum jacket is necessary to develop the full usefulness of any of the distilling tube packing combinations.

The tubes labeled "Standard Precision" are so termed because of their specific fractionating and refluxing lengths, and certain other details which have been standardized for use in a vacuum jacket described below; they will also be shown to be most effective for precise fractionation use. The "Regular" tube is taken from the Regular low-temperature vacuum-jacketed fractionating column previously described (*19*). The "Semi-Regular" tube is introduced only for the purpose of determining the liquid hold-up of the triple seal of the Regular tube. The "spiral" tube is part of a spiral vacuum-jacketed column constructed to the dimensions and specifications of the modification described by Davis (*9*). Drippers were constructed on the bottom ends of all the tubes except the 12.5-mm. inside diameter tube, as otherwise drops of liquid would tend to collect at the ends and obstruct the vapor passage.

Description of Packings. The wire coil and flat-strip coil packings were made of dimensions and pitch as seemed best from previous experience. Changes in size of wire or pitch, or in the spacing of the inner and outer coil, or both, would of course affect the characteristics of the packing, depending on the extent of the changes. To a considerable extent the effect of such changes can be estimated from the experimental data.

Other packings or distortions of the glass wall of the distilling tubes were not tried. It was not intended to survey all known packings, but merely to evaluate those which promised best fractionation.

Experimental Determination of Hold-Up of Liquid. The hold-up of liquid on the walls and packings was determined experimentally by carefully pouring exactly 10 cc. of c. p. toluene from a buret into the top of the exactly vertically aligned distilling tube, and measuring (in a 10-cc. finely graduated buret) all the liquid drained from the bottom of the tube after one minute of time elapsed from the pouring of the 10 cc. From three to eight or more such tests were made on each tube and packing combination, and the average of all readings was taken, except those obviously in error. The draining period of one minute was chosen as it most nearly represented the condition of wetness of column packing found

Table I. Experimental and Computed Data on Hold-Up, Maximum Distilling Capacity, and Factors 4 and 5 Ratings on Various Distilling Tubes and Packings (*Continued*)

Description of Distilling Tube	Characteristic Properties[1]	No Packing	Single-Wire Coil Packing	Double-Wire Coil Packing	Helical Flat-Strip Packing	Jack Chain Packing	Glass Cylinder Packing
F. Spiral distilling tube 5 mm. inside diameter, 400-cm. distilling tube length	*a*[2]	2.68	...	...	..	...	..
	b	0.389	...	...	..	...	..
	c	0.00	...	...	..	...	..
	d	3.069	...	...	..	...	..
	e	0.170	...	...	..	...	..
	f	0.042	..	...	..	...	..
	g	0.212	...	...	..	...	..
	h	2.857	...	...	..	...	..
	i	7.02	...	...	..	...	..
	j	4.07	...	...	..	...	..
	k	0.303	...	...	..	...	..
G. Standard Precision distilling tube 6.4 mm. inside diameter	*a*	0.44	1.30	1.67	1.22	...	..
	b	0.17	0.171	0.171	0.171	...	..
	c	0.00	0.012	0.018	0.019	...	..
	d	0.61	1.459	1.823	1.372	...	..
	e	0.066	0.066	0.066	0.066	...	..
	f	0.026	0.026	0.026	0.026	...	..
	g	0.091	0.091	0.091	0.091	...	..
	h	0.520	1.368	1.732	1.281	...	..
	i	24.0	14.75	10.8	6.9	...	..
	j	0.217	0.927	1.6	1.86	...	..
	k	0.0380	0.0618	0.0845	0.132	...	..
H. Standard Precision distilling tube 7.8 mm. inside diameter	*a*	0.61	1.77	2.23	2.13	3.40	..
	b	0.254	0.254	0.254	0.254	0.254	..
	c	0.00	0.014	0.021	0.029	0.040	..
	d	0.864	2.010	2.463	2.354	3.614	..
	e	0.092	0.092	0.092	0.092	0.092	..
	f	0.035	0.035	0.035	0.035	0.035	..
	g	0.128	0.128	0.128	0.128	0.128	..
	h	0.736	1.883	2.335	2.227	3.486	..
	i	36.3	26.5	21.20	14.5	8.4	..
	j	0.203	0.71	1.1	1.53	4.15	..
	k	0.0351	0.0481	0.0601	0.088	0.152	..
I. Standard Precision distilling tube 12.5 mm. inside diameter	*a*	1.17	...	...	..	4.92	7.15
	b	0.651	...	...	..	0.651	0.651
	c	0.00	...	...	..	0.114	0.134
	d	1.821	...	...	..	5.457	7.667
	e	0.174	...	...	..	0.174	0.174
	f	0.098	...	...	..	0.098	0.098
	g	0.272	...	...	..	0.272	0.272
	h	1.550	...	...	..	5.186	7.396
	i	106.0	...	...	..	32.50	21.60
	j	0.146	...	...	..	1.60	3.42
	k	0.0256	...	...	..	0.0835	0.126

by actual experience to be most conducive to good fractionation. The resulting data are plotted on log paper (Figure 2) and seem to correlate very well, considering that the different wire-coil and flat-strip packings were not strictly similar with respect to column diameter.

The unpacked Regular (*C*) and Semi-Regular (*D*) tubes show much higher hold-ups than the corresponding 3.8-mm. inside diameter Standard Precision (*E*) tube; and the Regular tube has higher hold-up than the Semi-Regular. These differences can be due only to the higher hold-up of liquid in the larger condensing tubes of the Regular and Semi-Regular tubes, and in the triple-wall seal of the Regular as against the Semi-Regular tube. The spiral tube (*F*) shows a very high liquid hold-up, due in part to the extra length (400 cm.) of the fractionating length proper as against the length (101.6 cm.) of the other tubes; but due mostly to the increased surface of the large condensing tube (7.8 mm. inside diameter) and capillary action of the triple-wall glass seal. Contrary to the statements of Davis (*9*) and Young (*28*), an inclined spiral tube holds up much more liquid (rather than less) than a vertical tube of same uncoiled length and bore. The single-wire coil and helical flat strip show least hold-up of all the packings, with the double-wire coil next in order. The jack chains show a much higher proportionate hold-up, while the glass cylinders hold up an abnormal amount of liquid compared with all other packings. For the unpacked tubes or for tubes packed with practically similar packings, the liquid hold-up seems to vary directly as the 1.6th power (approximately) of the distilling tube diameter.

Tubes *A* and *B* show erratic behavior due to the use of wire coils dissimilar to those used in the larger tubes and to the increasing effect of capillarity in these small diameters. Unpacked tube *A* tends to fill with liquid, instead of draining smoothly. The apparent discrepancy between the 2.6-mm. and the 3-mm. inside diameter single-wire coil packed tubes is due primarily to difference in the number of turns of wire per unit of length, and can be greatly lessened by using a packing with fewer turns.

Computation of Hold-Up of Material in Vapor Form. Inasmuch as the column holds up material in vapor as well as in liquid form, the hold-up of material in vapor form was computed from the dimensions of the distilling tubes as shown in Table I. A factor of 1/225 was used to convert vapor to liquid, as explained below. It should be observed that the hold-up of material in vapor form is by no means inappreciable, whether in the fractionating or in the reflux section.

Young (*28*) shows similar results of experiments on the liquid and vapor hold-ups of various distilling tubes; however, his values for unpacked distilling tubes of various lengths and bores are erratic when plotted as in Figure 2, and are in some instances more than 100 per cent greater or smaller than the present results. Inasmuch as the method used in the present investigation is a direct and accurate one, involving only measurement of liquid in finely graduated burets, and the results obtained are highly concordant when plotted, it must be concluded that Young's data are considerably in error, or at least not run under standardized conditions.

Computation of Hold-Up in Reflux. The hold-up of liquid in the condensing section of each distilling tube is computed either by proration of the total liquid hold-up in the case of the Standard Precision tubes, *A*, *B*, *E*, *G*, *H*, and *I*, or by suitable comparison of tubes *C*, *D*, *E*, and *F*. The hold-up of vapor is computed from the dimensions, using the factor of 1/225 to convert volume to cubic centimeters of liquid. Upon inspection of figures under *g* in Table I, it will be noted immediately that tubes *C*, *D*, and *F* have a hold-up far greater than corresponds to their distilling tube diameter. This fact is of great importance as will be apparent from the discussion under factor 5.

Experimental Determination of Maximum Distilling Capacity. Direct test of maximum distilling capacity by distillation of a test compound or mixture is very uncertain and unreliable unless the variables of sample composition, column temperature, column and still insulation, etc., are exactly fixed and measured. Essentially, maximum distilling capacity is fixed by the amount of liquid which can be coursed down the column without priming against an upcoming vapor of quantity bearing a fixed volumetric relation to the quantity of reflux liquid. It seemed, therefore, far

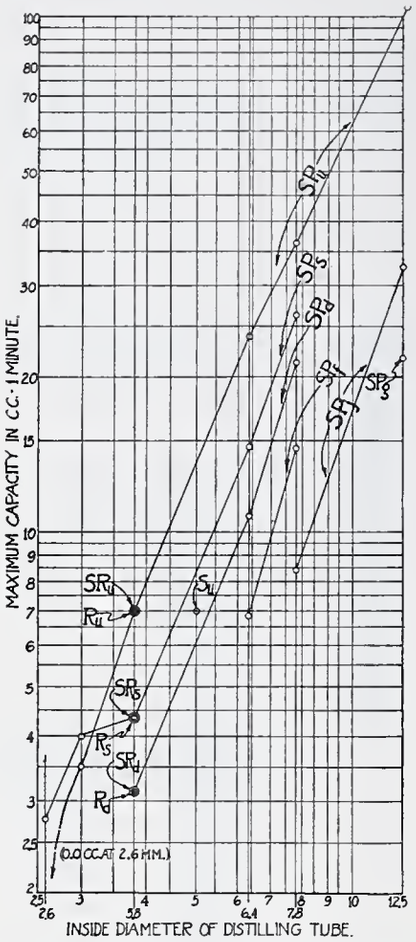

FIGURE 3. EXPERIMENTALLY DETERMINED MAXIMUM DISTILLING CAPACITY OF VARIOUS DISTILLING TUBE AND PACKING COMBINATIONS

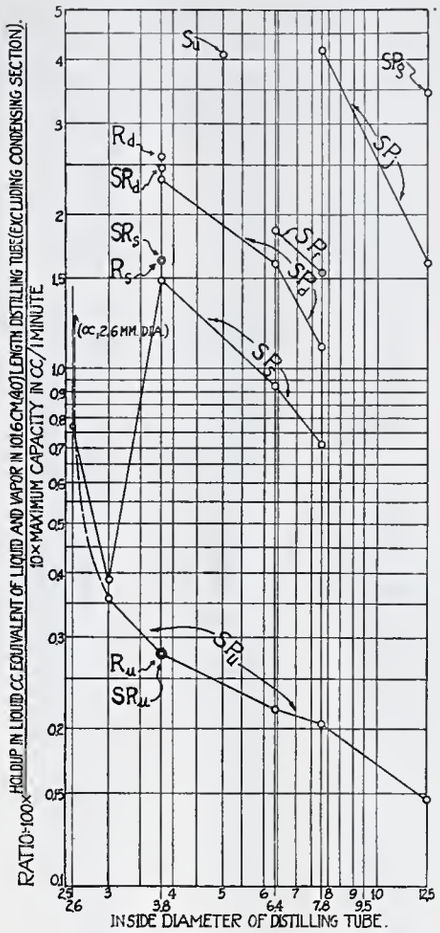

FIGURE 4. FACTOR 4 RATINGS FOR VARIOUS DISTILLING TUBE AND PACKING COMBINATIONS

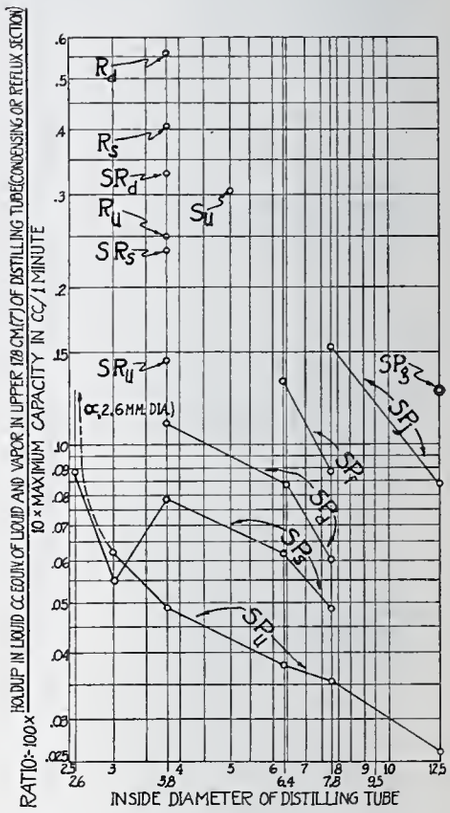

FIGURE 5. FACTOR 5 RATINGS FOR VARIOUS DISTILLING TUBE AND PACKING COMBINATIONS

SP, Standard Precision distilling tubes. *R*, Regular distilling tube. *SR*, Semi-Regular distilling tube. *S*, spiral distilling tube. Subscripts: *u*, unpacked. *s*, single-wire coil. *d*, double-wire coil. *f*, flat-strip coil. *j*, jack chains. *g*, glass cylinders.

preferable to use and to standardize permanently on a much simpler and what is believed to be a more positive and reliable determination of maximum distilling capacity, as follows:

Toluene is poured into the top of the column at a measured constant rate (using a mercury flowmeter for measurement), and simultaneously air is blown into the bottom of the distilling tube at a gradually increasing, exactly measured rate, until the column just begins to prime or flood. The rate of pouring the liquid toluene into the distilling tube is then changed, and the air flow again increased gradually, until incipient priming occurs. The quantity of toluene in cubic centimeters per minute is then plotted against the ratio of quantity of toluene in cubic centimeters per minute over quantity of air in cubic centimeters per minute required for incipient priming; and the resulting curve interpolated at a ratio of 1 cc. of toluene to 225 cc. of air, or to obtain the maximum vapor capacity of the distilling tube. A filter flask attached by means of a cork to the bottom end of the distilling tube is used to direct air flow and to collect the toluene draining from the column.

While the priming point is a very unstable phenomenon, easily affected by slight variations in the packing, by dirt on the packing, etc., the apparatus and procedure themselves are very simple. The actual determination of the priming point is difficult and requires some experience and skill. It was found that the best criterion is the first sign of periodic slugging or momentary complete entrainment of liquid en bloc in sections of the tube, followed by a burble of air dispersing the liquid. Such slugging would of course ruin the effectiveness of the column as a fractionating instrument. Maximum vapor capacity is taken as practically equal to the slugging point capacity thus determined. Above this point the column is unstable and priming is sure to occur at the slightest disturbance.

The factor of 1/225 is chosen to convert air volume to equivalent cubic centimeters of liquid because it can be shown that this ratio generally holds true for most liquids and their vapors at atmospheric boiling point temperatures, including the range of aliphatic hydrocarbons, ethane to octane and beyond. The objection may be raised that toluene at room temperature is not the same thing as a particular liquid sample to be distilled; nor is air the strict equivalent of a saturated vapor in contact with its particular equilibrium liquid. However, the usefulness of such a standard simple and easily reproducible test is apparent. Actually, the discrepancies introduced by the assumptions of this test are not great, and its findings have been well substantiated by actual distillations made with the distilling tubes and packings tested.

The various distilling tubes and packings, already described, were thus tested for maximum vapor capacity and the results incorporated under *i* in Table I and plotted on log paper in Figure 3. Tubes *C*, *D*, and *E* have about the same capacity within the limit of experimental error, as would be expected, although their liquid hold-ups are different. The capacities of the single-wire coil packed tubes are nearest to those of the unpacked tubes with double-wire coil, helical flat-strip coil, jack chains and glass cylinders following in order.

The order of capacities is the reverse of the hold-ups in Figure 2. The spiral tube shows an abnormally low capacity, just as it had previously shown an abnormally high liquid and vapor hold-up. This is, of course, due to the fact that the liquid draining down the spiral column does not have full gravity head and is therefore more easily entrained and slugged upward.

On the whole, the data fall on practically straight smooth curves, showing the substantial accuracy of the experimental determinations. Jack chains show both materially less

hold-up and materially higher capacity than glass cylinders, even though they present a great many more liquid-vapor contacts and changes of path per unit column length.

Tubes *A* and *B* are again erratic, for the reasons discussed above. The capacity of the unpacked tube *A* is zero, signifying flooding at no capacity; whereas the introduction of a fine wire spiral into the tube bestows upon it a fairly respectable capacity, due to the draining effect of the wire.

From the experimentally determined maximum capacities it is possible to approximate the minimum time of distillation required for a sample of a given size distilled in one of the tube and packing combinations tested; or conversely, to determine the maximum size sample which can be distilled in a given total time of distillation. An average reflux ratio of 6 to 1 may usually be assumed for routine determinations, yielding a sample size of 43.6 cc., for each hour of total time of distillation, in the case of the 3.8-mm. Standard Precision single-wire coil packed tube; and 212 cc., for each hour of total time of distillation in the case of the 7.8-mm. Standard Precision double-wire coil packed tube. (All cc. figures given in this paper are in liquid equivalent unless otherwise stated.) Much higher average reflux ratios may, of course, be used for precise work with corresponding diminution in size of sample per hour total time of distillation.

The maximum capacity figures are thus an index to the distilling capacity of the column. However, as regards the size of the intermediate fraction per cent, the criterion of sharpness of separation used in this paper, neither the maximum capacity figure *i*, nor the total hold-up figures, *h* and *g*, are of any significance. It is the relation between the hold-up and maximum capacity that is both significant and important.

Derivation of Factors 4 and 5. From the data thus far presented and incorporated in Table I, it is possible to compute factors 4 and 5 as listed under *j* and *k*, respectively, in the table. In order to give these factors a more immediate physical significance, the maximum capacity was multiplied by 10 to represent, roughly, the size sample which would be taken for a total time of distillation of 2 or 3 hours; and the quotient of the hold-up figure over ten times maximum capacity, in turn, multiplied by 100 to represent the percentage of the hold-up in terms of the sample size as assumed.

In the case of factor 4, the percentage figure thus obtained must be considered together with the rating of factor 6 before any final conclusions can be made. In the case of factor 5, the percentage figure indicates the minimum obtainable size of intermediate fraction regardless of all other considerations. The final percentage figures for factors 4 and 5 are plotted on logarithmic cross-section paper in Figures 4 and 5, respectively.

General Discussion of Factor 4. Factor 4 includes both the hold-up of liquid in the fractionating section as the numerator and maximum capacity as the denominator. Its value may therefore be decreased either by decreasing the hold-up in the fractionating section, *h*, by using a low hold-up packing or maintaining the packing barely wet in operation, or by increasing the column capacity, *i*. For two columns, which are approximately equal in scrubbing effectiveness as discussed under factor 6, their rating in terms of factor 4 is an inverse quantitative (and approximately linear) measure of the sharpness of separation that may be secured at the top of the column packing for the same sample and conditions of operation. Figure 6 serves graphically to illustrate this statement, which follows from theoretical considerations as reviewed in Young's book (*26*), and from the nature of the criterion of column effectiveness as defined in this paper, namely, least intermediate fraction per cent in least total time of distillation (without regard to sample size). For the two columns, *A* and *B*, as shown, the composition and temperature gradient are exactly the same. Both columns are assumed to have the same sample capacity, and hence the size of sample is the same for both. However, the size of the intermediate fraction as shown on the corresponding fractional distillation curves above the columns is widely different—column *A* is three times as effective as column *B*. It is not necessary for the general truth of this relation that the separation between components be as sharp as indicated in the illustration. Factor 4 is not distinguished by a determination of the height of equivalent theoretical plate (H. E. T. P.) as described by Peters (*18*) and Carswell (*7*); nor by any procedure for determining the effectiveness of a column which is based only on the composition and temperature gradient throughout the column.

It is interesting to compare the relative importance of factor 4 as defined and of factor 6, which expresses the scrubbing effectiveness of the column. It is well known from general

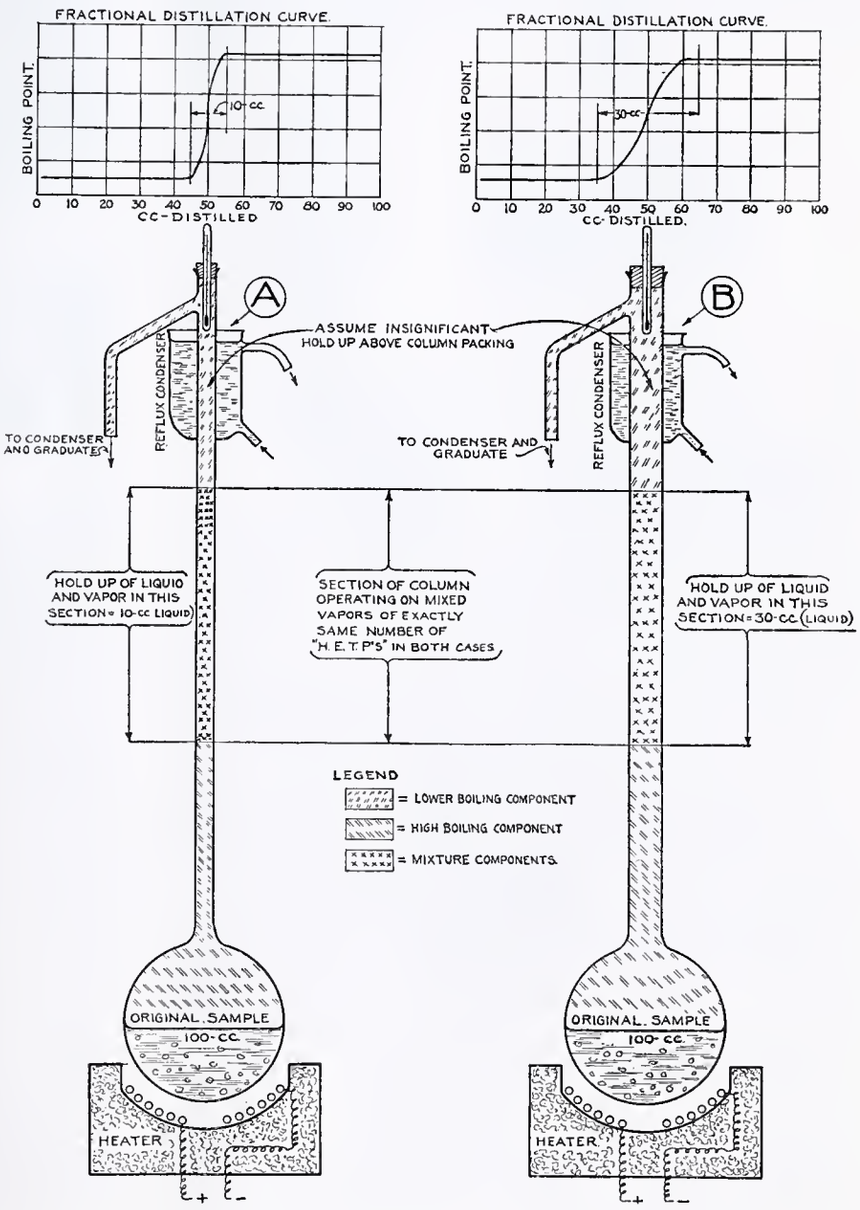

Figure 6. Effect of Difference in Factor 4 Rating

fractional distillation theory that increasing the number of plates or the height of a column follows a law of diminishing returns—i. e., the contribution of each added plate to scrubbing effectiveness is less than that of the preceding one. However, it is perhaps apparent from inspection of Figure 6 and from general considerations that the decrease of the intermediate fraction per cent with decrease of factor 4 rating is substantially linear.

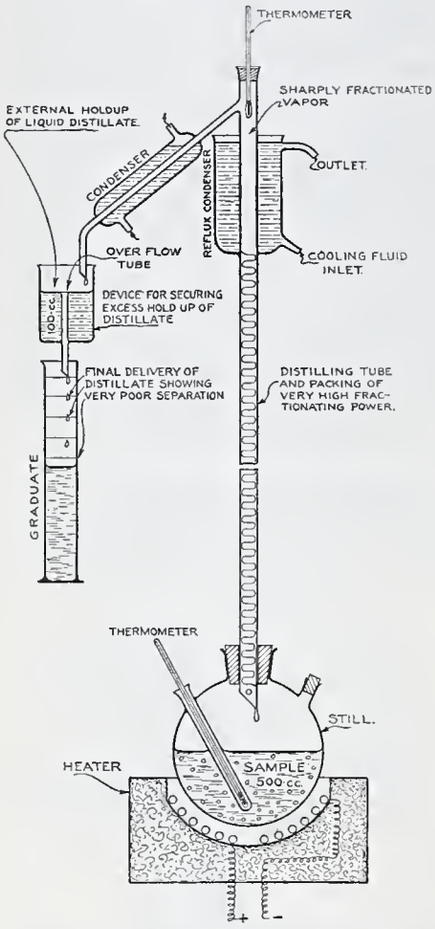

Figure 7. Effect of High Factor 5 Rating

Furthermore, the rating of factor 4 is a limiting one on the effectiveness of a column, inasmuch as even an infinite increase in column height cannot change the ratio of change of composition accomplished per unit length column to the hold-up of material per the same unit length column. The practice in laboratory column design intended for sharpest possible separation as for the study of petroleum composition, of going to extreme heights (up to five and more stories, *5*, *14*) is not as likely to achieve its object as the lessening of hold-up per unit length of column to the utmost minimum compatible with retaining scrubbing effectiveness and sufficient capacity.

Referring now specifically to the data presented in Table I and Figure 4, it is apparent that factor 4 tends to decrease for the larger diameter Standard Precision tubes, indicating that the larger tubes are inherently more effective than smaller ones for packings of equal scrubbing effectiveness. This is, of course, due to the fact that the total hold-up increases as between the first and the second power, whereas maximum capacity increases somewhat faster than the second power of the diameter. As a matter of fact, in high-temperature distillations, where distilling tubes up to 8 mm. inside diameter and larger are used with correspondingly larger samples, components boiling as little as 2° and 3° C. apart can be distinguished (Figure 6, Part III), which is extremely difficult to do with 3.8-mm. inside diameter and smaller tubes as used in low-temperature fractionation.

The unpacked tubes have very much lower values for this factor than the packed ones. This is not in disproof of the importance of factor 4, but on the contrary shows a real advantage of unpacked tubes which must be compensated for and more than compensated for by a large increase in factor 6 in the case of unpacked *vs.* packed tubes. However, in the case of tubes *A* (2.6 mm. inside diameter) and *B* (3 mm. inside diameter), the introduction of a fine wire spiral assists in draining the liquid which seems to have a tendency to be held up by capillarity in the unpacked tubes and, therefore, the single-wire coil-packed tube curve meets and intersects the unpacked tube curve somewhere between these two diameters.

The lower limit of diameter for the unpacked tubes seems to be reached at about 2.6 mm., as at this point the factor 4 rating is infinite, signifying inoperativeness. The unduly high rating of the single coil packed 2.6-mm. tube is due mostly to the large number of turns of wire per unit length, but even allowing for this it appears that smaller tubes than *A* would have greatly increased ratings of factor 4.

Tubes 2.6 to 3.0 mm. inside diameter may be used for precise analysis of gas or liquid samples as small as 0.3 cc. of liquid or 50 cc. or less of condensable gas and compare very favorably with the gas distillation analysis apparatus described by Rosen (*21*). (Ten cubic centimeters of a gas sample can be analyzed with a distilling tube of 2.4 mm. inside diameter and 25 cm. long.) A completely sharply defined fractional distillation curve may be obtained for a natural gas or gasoline sample in 1.5 to 2 hours and with a liquid air consumption of only a few hundred cubic centimeters. The unusual characteristics of the tubes are due to the fact that their diameters are sufficiently small so that highly efficient contacting of reflux liquid with vapor (factor 6) occurs even without any packing; as a matter of fact, the main function of packing is to prevent flooding by its draining effect, as a stirring rod facilitates pouring liquids from a beaker.

Spiral continuous packings appear to be much superior from the standpoint of factor 4 rating to other discontinuous and chance arrangement packings, such as Lessing and other rings, glass beads, jack chains, etc. The principle extends to all other forms of helical or even nonhelical continuous and geometrically uniform and symmetrical packings. The testing methods and reasoning presented in this paper for the first time (including tests for factor 6) are suitable for exact and conclusive determination of the merits of specific packings of all kinds.

For instance, Bruun (*3*) describes laboratory fractionating columns with actual glass bubble plates about 35 mm. outside diameter, also somewhat more compact designs of smaller diameters. It appears from the description that the rating of such columns for factor 4 is extremely high on account of the high hold-up and very low capacity, and that the use of a comparatively small number of bubble plates would not compensate for this shortcoming, inherent in this particular type of column design.

It appears from the above and other references in the literature that the importance of securing a low rating of factor 4, although readily demonstrable from both theoretical considerations and actual operation of a precise efficiently controlled column, has not been sufficiently appreciated.

General Discussion of Factor 5. It will be noted that tubes *C*, *D*, and *E* (Figure 1) have approximately the same rating on factor 4. In actual use, however, the 3.8-mm. inside diameter Standard Precision tube is several times superior to the 3.8-mm. Regular tube with identical packing and under same conditions. The reason for this very material discrepancy is to be found in differences in factor 5; which is the ratio of hold-up of material in the reflux or condensing section to the maximum capacity as plotted for all combinations in Figure 5. Tubes *C*, *D*, and *F* show a very high rating for this factor, whereas the Standard Precision tubes have a much lower rating. Apparently, in this case at least, factor 5 is far more influential than all the other factor variations combined.

Figure 7 is presented to illustrate the effect of excess hold-up of material in the reflux or condensing section of the column. In the figure such hold-up is secured artificially by the 100-cc. capacity overflow device shown. It is obvious that any separation accomplished in the column is completely lost by the reblending of the separated components before collection.

Exactly the same sort of thing occurs when such excess hold-up occurs within the condensing column section because of unnecessarily large condensing tube diameter or length, liquid occluding seals or crevices, devices for partitioning reflux, etc. While the fractionating column itself may have considerable hold-up of material per unit length, this is usually more than compensated for by the fractionating action of the packing. In the condensing section, the fractionating effect drops out, and any appreciable hold-up of material limits and in extreme cases practically destroys the fine separation of components existing at top of column packing. This point has not been sufficiently appreciated or emphasized by other workers with laboratory fractional distillation apparatus. Most column designs incorporate complicated seals, reflux proportioning devices, liquid seals, etc., which, in the light of the present experience and experimental work, are certain to ruin the efficiency actually obtained in the columns.

Bruun (*4*) describes a reflux regulator for laboratory stills which is open to the objection of excessive hold-up and in fact is similar to the exaggerated diagram of Figure 7.

Fitch (*15*) describes a modification of the Podbielniak low-temperature fractionating column, intended for the precise fractionation of very small gas samples which has a 2.7-mm. inside diameter distilling tube packed with a fine wire spiral as tested in this investigation, but which has a 5-mm. inside diameter condensing tube and a bulky triple-wall seal similar to distilling tube *C* in Figure 1. The hold-up in the reflux section is sufficient to offset the advantages of the small-diameter distilling tube used. There is no provision for controlling the volume of the distilling bulb, as by admission of mercury.

Furthermore, this point has not been carefully considered in the experimental comparisons of fractionating columns by other investigators and undoubtedly slight modifications of the upper column design have had profound effect on the results considered representative of the columns.

Factor 6. Scrubbing Effectiveness of Column Packings

Comparison of Packings. The desirability of securing most effective possible scrubbing action between the descending reflux liquid and the ascending heater vapor from the still by the use of suitable column packing is well recognized. The data and discussion under factors 4 and 5 show the advantages of packings based on perfect uniform, continuous, and geometrically symmetrical construction over all the chance arrangement packings, including cylinders, rings, jack chains, etc., and over the discontinuous modifications and inserts on the glass walls, as regards least liquid hold-up and maximum capacity for least column diameter.

It is perhaps evident from inspection alone that the spiral packings can be made to give materially better scrubbing action than the other packings. Actual comparison of these packings with Lessing rings, jack chains, glass cylinders, etc., by distillation in the same apparatus on same sample and with same operational variables demonstrates their superiority. The separation obtained in a single distillation such as any of those illustrated in Figures 3 to 13 in Part III of this series is far better than sixteen redistillations in the Young and Thomas Evaporator (*26*). Curves with such sharp breaks for petroleum products have not been duplicated with other packings.

The wire packing described by Dufton (*12*) is also spiral, continuous, and uniform. However, its action is utterly unlike that of the wire-coil and flat-coil packings here described, inasmuch as the large-diameter wire is merely a spiral partition rather than a point of attachment for capillary films (factor 6). The use of glass tube or rod core is objectionable on account of difficulty in snug fitting of parts, high heat capacity and conductivity of the large-diameter glass tubing and of the wire, and, what is more important, the resulting large hold-up throughout both the fractionating and refluxing length of the column (factors 4 and 5). As a result, the Dufton column, while apparently similar to the distilling tubes here described, does not compare as to sharpness of fractionation which may be secured. This analysis of the Dufton column characteristics was confirmed by actual comparative distillations.

Determination of Factor 6. Factor 6 can be determined directly and separately from factors 4 and 5 by means of the following suggested general procedure:

A standard wash liquid is poured into the top of the column at a constant measured rate in countercurrent relation with a suitable standard vapor entered into the bottom of the column at a constant measured rate 225 times (by volume) greater than that of the standard wash liquid rate. By analysis of the enriched wash liquid or the stripped vapor or both, or by determination of some characteristic physical property such as density or refractive index, it is possible to determine quantitatively the scrubbing effectiveness of the column and its packing free from the effects of hold-up.

The test can be made at room temperature, thus eliminating the need for column insulation. The scrubbing effectiveness will vary to a certain extent with the ratio of the capacity of column actually used over maximum capacity, and it is interesting to determine this relation. As already mentioned, the packing should be barely wet for best fractionation; however, this is not necessarily the optimum condition for best scrubbing effect such as would be of value in continuous distillation. In other words, keeping the packing barely wet might generally improve separation through affecting factors 4 and 5 advantageously, although affecting factor 6 adversely. Experiments of this type are very useful and are recommended in the close comparison and design of packings; and the results when correlated with factor 4 should be completely reliable indications of the usefulness of the packing when incorporated in an adiabatic properly designed and operating column. Results of such tests will be described in another article of this series.

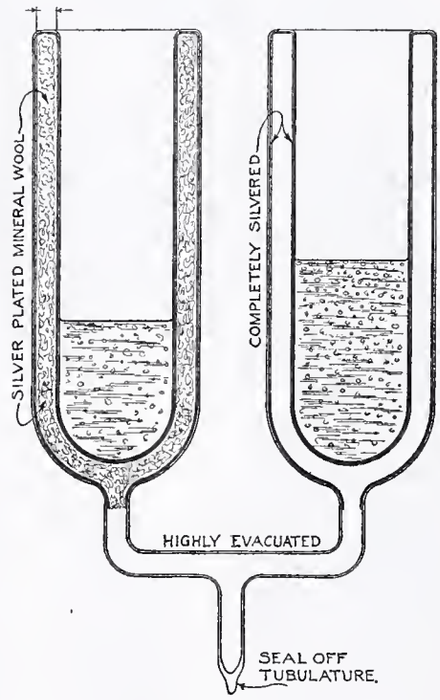

Figure 8. Experiment with Packed Vacuum Tube

Factor 7. Efficiency of Thermal Insulation of Column

The importance of securing sufficient thermal insulation in the case of small-diameter laboratory fractionating columns has been well understood theoretically, but there has been difficulty in securing such insulation in a practical manner.

Practically perfect thermal insulation is required in order to achieve sharp separation of components boiling only a few degrees Centigrade apart, inasmuch as even slight heat losses will completely disturb the delicate equilibrium of the column. What is more serious, at temperatures much below room temperature uninsulated columns will completely superheat; while at temperatures very much above room temperature the columns will flood unless the column diameter be made several times greater than would be necessary, resulting in high hold-up of liquid and vapor and consequent poor fractionation. Merely lengthening the column will obviously not compensate for poor insulation and may make matters worse. No matter how inherently well designed and constructed a distilling tube and its packing may be, its usefulness is materially limited by poor thermal insulation.

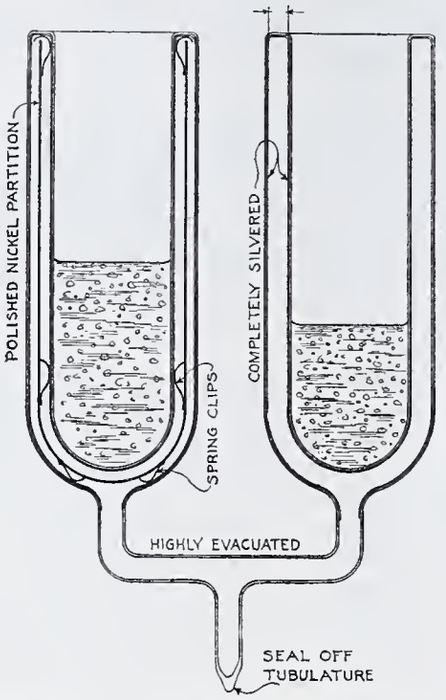

Figure 9. Experiment with Reflector Partition Vacuum Tube

Figure 16 shows various forms of fractionating columns, all except Peters' column 7 insulated with vacuum jackets. These columns incorporate the distilling tube and packing elements as shown separately in Figure 1 and discussed under factors 4, 5, and 6. Column 7 does not depend at all upon a vacuum jacket or other lagging, but upon the maintenance of an artificial external temperature gradient adjusted to match closely the internal natural temperature gradient. It has not been used for fractionations below room temperature, for the obvious reason that refrigerating and not heating wire coils would have to be used. The other columns have been used for low-temperature fractionations and could be used for reflux temperatures up to about 100° C.

Artificial External Thermal Gradient Insulation. The external artificial thermal gradient, although the only practical alternative to an efficient vacuum jacket, is not a precise device. Ordinarily the top and the bottom temperatures of the air flowing through the jacket cannot be maintained closer than 3° C. to the corresponding temperatures inside the column. It may, therefore, be presumed that a much greater variation of internal and external temperatures occurs in the body of the jacket. Furthermore, there is no simple way of determining how much the thermal gradient of the column is distorted from the gradient it would assume if perfect insulation could be obtained. The heat input to the jacket may be as much as 1400 watts, while the heat input to the still is not more than about 500 watts for a 12.5-mm. inside diameter tube, which shows the difficulties of regulation. The use of this type of insulation for the expected separation of components boiling only about 10° C. or less apart seems to be ineffective and, actually, such separation could not be accomplished in this type of column except with great difficulty.

Unsilvered and Strip-Silvered Vacuum Jackets. The strip-silvered vacuum jacket is fairly successful for low-temperature fractionations even down to liquid air temperatures. Some difficulty is experienced in the refluxing of methane, and it was believed that if better insulation were made possible it would result in sharper fractionation. For high-temperature distillations, above 100° C. and up to 300° C. where heat transfer by radiation becomes a more important mechanism than conduction or convection, even the strip-silvered vacuum jacket becomes inadequate and the unsilvered vacuum jacket almost completely useless. Furthermore, at the higher temperatures the differential expansion of the inner or distilling tube of the vacuum-jacket column, relative to the outer cool tube, invariably results in fracture of the glass.

The literature was, therefore, searched for information leading to an improvement of the vacuum-jacket type of column to make it more efficient for low-temperature work and applicable for high-temperature work.

Dewar (*11*) has made some very interesting experiments on filling the vacuum space between the walls of a vacuum container with various finely divided insulating powders, also with partitions of papers plated with tin, silver, and gold, and observing the

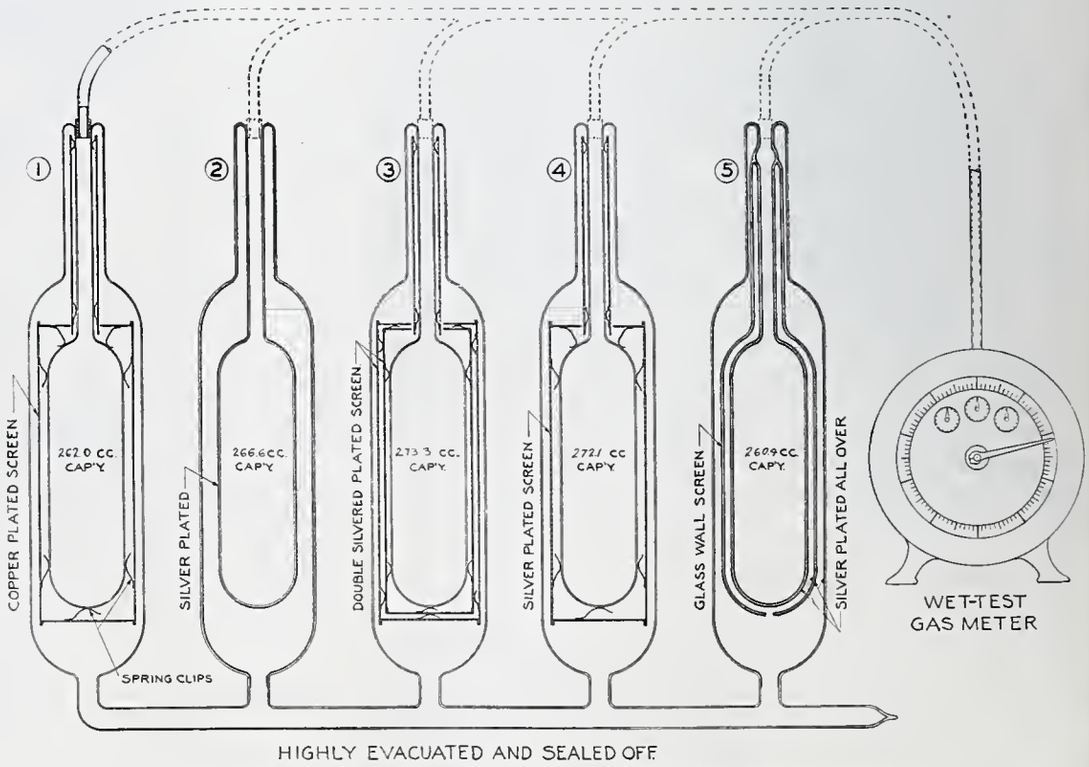

Figure 10. Experiment with Narrow-Neck Dewar Flasks

resulting thermal insulation effectiveness of the containers, compared with a silvered vacuum vessel as a standard. While these devices showed considerable improvement over a nonsilvered vacuum tube, nothing was found superior to the silvered vacuum vessel. Smoluchowski (*22*) discloses a vacuum vessel with the vacuous space filled with lycopodium powder and claims high insulating effectiveness. Banneitz, Gerbo, and Kurcze (*1*) give the results of very comprehensive experiments on the design and manufacture of vacuum containers. They find that silvered screens provided with minimum thermal contact with the walls of iron vacuum containers considerably improved the thermal insulating effectiveness of the containers. Fahnestock (*13*) and Bock (*2*) also disclose partitions in the vacuum space of vacuum containers, as an aid to insulation.

No reference was found to direct use in improving the insulating power of the vacuum-jacket type of container. Apparently the fully silvered, well-evacuated type of vacuum container was recognized as the most perfect insulator available. Experiments were therefore made to gain further information specifically pertaining to laboratory vacuum-jacketed fractionating columns.

vacuum secured was better than 0.00001 mm. of mercury; and a further improvement in vacuum had no appreciable effect on the vaporization rate, proving that the residual leakage of heat across the evacuated spaces of the tubes occurred almost entirely by radiation and not by molecular activity. The rate of vaporization of liquid air was measured by successively connecting each tube with rubber tubing to a wet test meter and noting with a stopwatch the time required to liberate a unit volume of liquid air vapor. To avoid any error which might be caused by lack of uniformities in the meter drum, the unit volume of air was always measured between identical graduations on the circular meter scale. Table II summarizes the experimental data leading to a final quantitative comparison of insulation efficiencies, taking the silvered partitionless tube as 100 per cent efficient.

In considering these experimental results, it should be noted that the metal reflector-type partitions were somewhat crude, in that they were not well polished and there were numerous open chinks between joints. On the other hand, tubes 2 and

Table II. Comparison of Thermal Insulation Effectiveness of Vacuum Containers[a] in Terms of Time Required to Vaporize Equal Quantities of Liquid Nitrogen

	Description	Capacity[b] Up to Bottom of Neck	Actual Time	Time Corrected for Inequality in Amounts of Liquid Air Vaporized	Insulating Effectiveness (No. 2 = 100%)
		Cc.	*Min.*	*Min.*	%
1	Single metal reflector, copper-plated inside and outside	262.0	2640	2626	66
2	Conventional Dewar container, silvered on all inside walls	266.6	3975	3980	100
3	Double metal reflector, silvered all over, glass walls not silvered	273.3	3856	3767	95
4	Single metal reflector, silvered inside and out, glass walls not silvered	272.1	2935	2878	72
5	Triple-walled container with glass partition sealed to upper extremity of neck, all inside walls, including partition, silvered	260.4	4625	4688	120

[a] Approximate internal dimensions, 1.125 in. (2.86 cm.) × 8 in. (20.4 cm.)
[b] Average capacity of five containers, 266.9 cc.

Packed Vacuum Tubes. It was decided to try out an improved form of finely divided packing material in the vacuum space of a vacuum tube. Mineral wool is known to be a very efficient insulator. Mineral wool was therefore silver-plated to improve its reflecting power and two comparison thermos tubes prepared, as shown in Figure 8, both tubulated to a mercury vapor pump. Both tubes were filled with the same amount of liquid air and the rates of vaporization noted. At poor vacuum the mineral-wool-filled tube was superior; but when the vacuum improved the silvered tube proved to be much better. Apparently, when the pressure was low enough so that the transfer of heat by conduction and convection in the residual air became relatively insignificant, the transfer of heat by conduction along the contacting fibers of the glass wool was more than enough to offset the advantages of multiple reflection of radiant heat. It was therefore decided to discard the packed type of vacuum container. Undoubtedly, some of the results of previous investigators of packed Dewar tubes are unreliable because of insufficient evacuation of the tubes, and resulting faulty comparisons.

Reflector Partition Vacuum Tubes. Another pair of tubes was tried out as shown in Figure 9. The tube on the left was provided with a thin polished nickel partition spaced apart from the glass walls except for a minimum amount of spacing plugs of glass wool. Both tubes were again filled with equal quantities of liquid air and rates of vaporization noted. This time the nickel partition tube proved about 20 per cent superior to the silvered tube; that is, it kept liquid air 20 per cent longer. This preliminary experiment was sufficiently encouraging to justify setting up a series of five vacuum tubes each of approximately 260 cc. capacity to bottom of neck with long narrow necks, as shown in Figure 10. A high vacuum was secured and maintained by means of a mercury vapor pump operating continuously. The degree of

5 were practically perfectly silvered. Undoubtedly much better results could be obtained for the metal reflector tubes by better workmanship, and the results of the experiments should be interpreted with this fact in mind.

Comparison of tubes 2 and 5 is particularly interesting, as both these tubes are very well silvered and represent highest insulating efficiency possible for their respective types. Tube 5 is 20 per cent superior to tube 2 in thermal insulation. However, according to theory (*1*, *10*, *25*), it should be 100 per cent more efficient. The only conclusions possible are that either the theory is at fault or the conduction of heat along the necks (including the neck of the partition) of these comparatively small-capacity tubes was sufficient to reduce materially the contrast between the respective insulation efficiencies of tubes 2 and 5. Obviously, further experimental work had to be done to determine the cause of the poor results on the partitioned thermos containers. Such experiments will be described in a later paper.

Vacuum-Jacketed Columns. For the purpose of the investigation of vacuum-jacketed fractionating columns, these preliminary experiments served to indicate that a single or double or possibly multiple reflecting partition type of vacuum jacket would be materially superior to a plain silvered jacket. It is easily possible to perforate metal reflectors in any desired way to provide maximum visibility of the column packing and reflux with least total area of perforations. Silvering of glass is very limited in this respect. It was therefore decided to construct a series of sleeve-type vacuum-jacketed columns, one each, completely silvered, strip-silvered, equipped with single nonperforated reflector, with single reflector perforated for visibility, etc., and to test them in comparison with each other by determining the actual leakage of heat through the walls of the jackets at various internal temperatures. The testing principle used was that of inserting standardized uniform-resistance heating coils

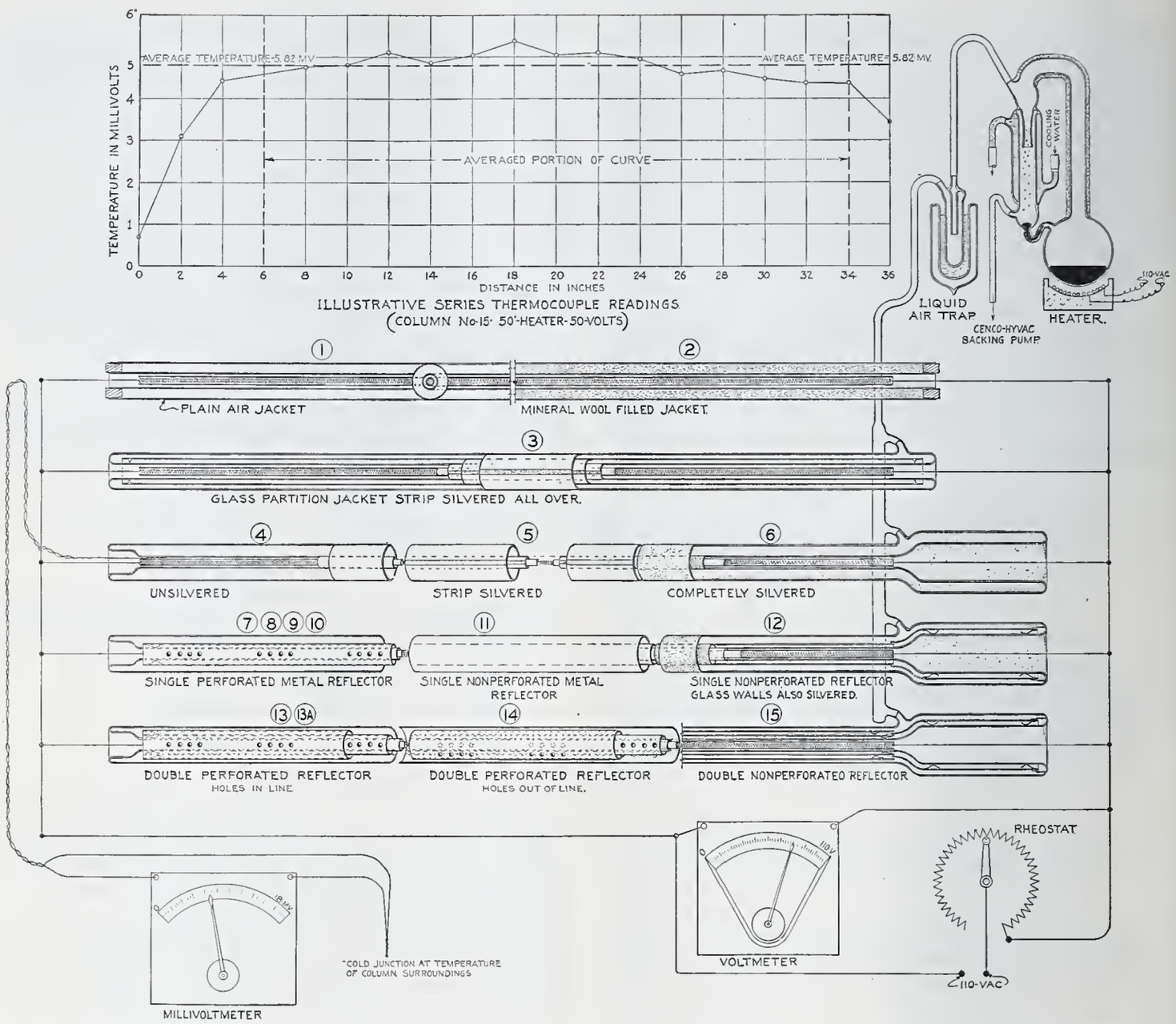

Figure 11. Diagram of Experimental Apparatus for Testing Vacuum Jackets and Other Types of Column Insulation

1. Plain air jacket composed of inner Pyrex tube, 9 mm. inside diameter and of outer Pyrex tube about 36 mm. outside diameter, spaced at ends with corks, as shown
2. Same as 1, but with mineral wool loosely packed into annular space between inner and outer tubes
3. Same as 1 in dimensions of inner and outer tubes, but provided with glass tube partition as shown, the whole interior including partition silvered completely except for clear strip 0.25 inch (0.63 cm.) wide, extending lengthwise of entire tube; ends of this tube sealed in ring seals as shown and tube provided with tubulature and connections to high-vacuum pump
4. Sleeve-type jacket for fractionating column, inside diameter about 9 mm., outside diameter of outer tuber about 35 mm., interior evacuated but not silvered
5. Same as 4, but interior silvered completely except for clear strip about 0.25 in. wide (0.63 cm.) extending lengthwise of entire tube
6. Same as 4, but interior completely silvered
7. Same as 4, but provided with special nickel-chromium iron alloy reflector tube, highly polished, 0.56 in. (1.44 cm.) diameter, 0.004 in. (0.01 cm.) thickness walls; perforated for visibility as shown, perforations 0.25 in. (0.63 cm.) diameter; occur in sets of 4 on 0.375 in. (0.95 cm.) centers, 1.75 in. (4.44 cm.) space between sets, holes matching diametrically on both sides of tubes. Total number of holes, 104
8. Same as 7, but copper-plated inside and outside
9. Same as 7, but silvered outside only
10. Same as 7, but silvered both inside and outside
11. Same as 7, but reflector not perforated; silver-plated inside and outside
12. Same as 7, but reflector not perforated; silver-plated inside and outside. Glass walls silvered on all interior surfaces
13. Same as 7, but reflector silver-plated inside and outside; provided with additional concentric 0.875 in. (2.22 cm.) diameter reflector, perforated to match holes with inner reflector and silver-plated inside and outside

13A. Same as 13, but with 80 perforations and very highly polished
14. Same as 13, but reflectors turned so that perforations are not in line
15. Similar to 13 and 14, except that reflectors are not perforated

in all the jackets, applying a constant definite voltage to the terminals of the coils to form heat within the jackets, and measuring all temperatures at intervals of exactly 2 inches along each jacket with a calibrated exploring thermocouple. The heating coils were made of No. 36 nichrome wire, wound as uniformly as possible on a 0.125-inch (0.318-cm.) mandrel, exactly 40 inches (102 cm.) in over-all length when coiled, and made in actual uncoiled lengths of 5, 10, and 50 feet (152, 305, and 1524 cm.), respectively, for various heat requirements. In practice, it was found that several hours were needed to establish equilibrium in the rate of heat leakage and internal temperatures. Description and details of the testing apparatus are given in Figure 11 which is drafted so as to be practically self-explanatory.

A curve of test data is given in Figure 11 for column 5. It will be noted that the temperatures drop off considerably towards the ends of the column, because of conduction along both the metal of the reflector and of the glass in the inner tube of the column. However, the metal reflector tube was sufficiently thin and constructed of very low heat-conductivity

metal alloy (one-thirtieth the conductivity of silver), so that this conduction towards the ends is not greater than for a heavy deposit of silver on the glass walls. In a fractionating column this slight conduction of heat towards the reflux and towards the still would not exist, because the still and reflux, respectively, would maintain temperatures in conformity with the general thermal gradiant throughout the column. Therefore the average internal temperature was taken over that part of the curve comprising over 75 per cent of it (see vertical lines in plot) which showed no appreciable end effect.

It was also obvious from the curves for temperatures throughout the individual columns that the heating coils used were not quite uniform throughout their length and that this nonuniformity affected the temperatures considerably. However, the average temperature of the interior of the column was practically constant no matter which heating coil was used or whether the same heating coil was inserted first one way and then reversed for another experiment. It was therefore not considered necessary to repeat the experiments with more uniformly wound coils.

The experimental results are summarized and graphically compared in Figures 12, 13, and 14. The numbers on the curves correspond to the reference numbers and description as given under Figure 11. On account of experimental difficulties in obtaining a sufficient number of points, some of the curves are extrapolated beyond about 200° C., with consequent uncertainty in the higher temperature region, but, it is believed, without affecting the conclusions made from the

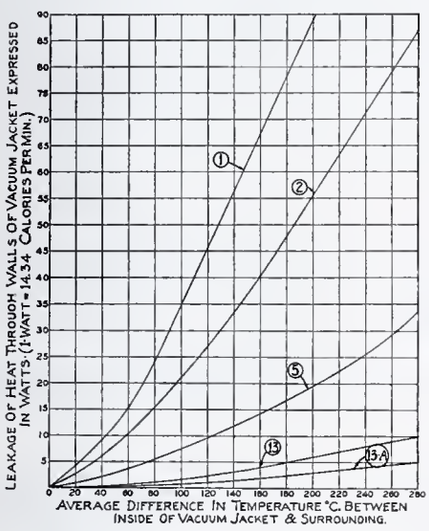

FIGURE 12. RESULTS OF EXPERIMENTS ON EFFICIENCY OF COLUMN INSULATIONS. JACKETS 1, 2, 5, 13, AND 13A, FIGURE 11

1. Plain air jacket, inner tube 9 mm. inside diameter, outer tube 36 mm. outside diameter
2. Same jacket as shown in 1, but annular space of tube filled with mineral wool insulation
5. Vacuum jacket silvered solid, except for 0.188 to 0.25 in. (0.45–0.63 cm.) clear strip running lengthwise on both sides for visibility
13. Double reflector jacket, suitably perforated for visibility
13A. Same type vacuum jacket as 13, but of improved construction

comparisons of different jackets. No attempt will be made to discuss the significance of these results as bearing upon the theory of multiple-walled vacuum containers, as this will be discussed in a later paper. However, the following conclusions suggest themselves as of importance in the design of laboratory fractionating columns. It is to be understood that these conclusions apply strictly only to the particular types of vacuum jackets tested in the manner described, and broader application of the conclusions may be made only with great caution.

1. Plain air-jacket insulation or insulation with mineral wool, asbestos fiber, etc., is of little benefit and utterly inadequate for fractional distillations at temperatures far removed from room temperature, unless the column is made many times larger in cross section than actually needed for an adiabatic column.

2. An unsilvered vacuum jacket is less than one-third as effective a thermal insulator as a jacket silvered all over except for a narrow strip left clear for visibility; and not much superior to mineral wool insulation.

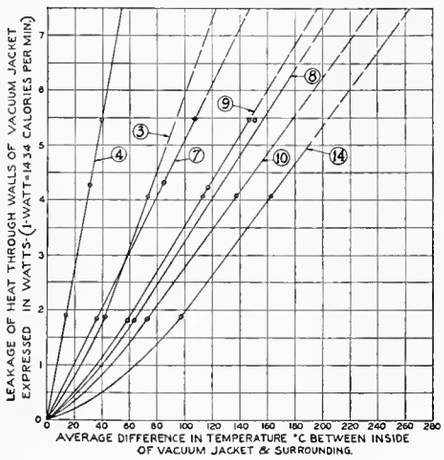

FIGURE 13. RESULTS OF EXPERIMENTS ON EFFICIENCY OF COLUMN INSULATIONS. JACKETS 3, 4, 7, 8, 9, 10, AND 14, FIGURE 11

3. Glass partition strip silvered
4. Evacuated unsilvered
7. Unplated perforated nickel-chromium reflector
8. Reflector perforated and copper-plated
9. Reflector perforated and silver-plated outside only
10. Reflector perforated and silver-plated both sides
14. Double perforated reflector, holes out of line

3. After a certain point, further evacuation of any type vacuum jacket is not effective in further improving the insulation as radiation becomes the main mechanism of heat transfer through the walls. However, this point corresponds to very much lower pressures in the case of the better screened vacuum jackets than in the case of the unsilvered or poorly screened jackets.

4. The completely screened vacuum jackets, such as the completely silvered ones or those having unperforated single or double reflectors in the vacuum space, are as a class materially superior to jackets having clear strips or perforations for visibility, even though the area of such screened openings is but a very small fraction of the total area of the reflecting screen means.

5. Within the completely screened vacuum-jacketed group, the single reflector partition is practically equivalent in thermal insulation to a completely silvered jacket, while the double reflector partition is 16 per cent more efficient, and a single reflector partition plus complete silvering of glass walls is 25 per cent more efficient than a completely silvered jacket. The thermal insulation of this group is so nearly perfect that even very slight conductance of heat towards the ends tends to equalize the ratings of the members of the group.

6. Within the visible group (provided with clear strips or with perforations for visibility), the single reflector is about twice as good an insulator as the best strip-silvered vacuum jacket, while the double metal reflector is from two and a half to four times as good an insulator as the best strip-silvered vacuum jacket. There is considerable room for improvement in the reflector-type jacket by cutting down on perforation area, improving the silvering, and in other ways, while the practical limit of efficiency seems to have been reached in the strip-silvered jacket.

7. The leakage of heat through the walls of the vacuum jacket at an internal average temperature of 300° C. for single and double perforated reflector-type vacuum jackets ranges from an estimated maximum of about 15 watts to as low as 5 watts.

8. The air at atmospheric pressure present in the annular clearance between outside wall of heating coil and inside wall of vacuum-jacket sleeve does not seem to have an appreciable effect as regards longitudinal conduction of heat.

Application of Results to Low-Temperature Fractionations. From the above conclusions it appears that either a single or double silver-plated perforated reflector-type vacuum jacket presents a material improvement over a strip-silvered vacuum jacket. From actual tests it was found that a single metal reflector jacket considerably improved the performance of low-temperature fractionating columns as

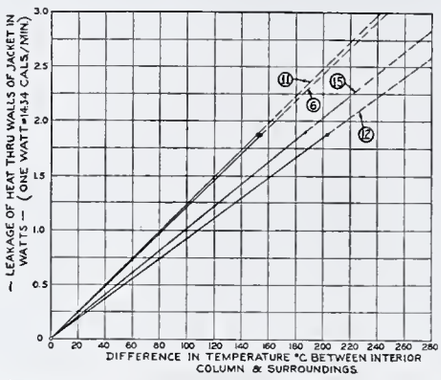

Figure 14. Results of Experiments on Efficiency of Column Insulations. Jackets 6, 11, 12, and 15, Figure 11

6. Silvered on glass walls, no reflector
11. Single nonperforated reflector, silver-plated
12. Single nonperforated reflector, silver-plated; glass walls silvered
15. Double nonperforated reflector, silver-plated

regards ease of entering high methane percentage samples, refluxing methane, and obtaining sharpest possible breaks. From considerations of the greater cost of the double reflector construction, it was concluded that for low-temperature work the single reflector jacket furnished substantially perfect insulation together with sufficient visibility. Extensive experience in many laboratories with these perforated reflector-type vacuum jackets substantiates their material superiority over the strip-silvered jackets.

Application of Results to High-Temperature Fractionations. For distillations at temperatures above about 150° or 200° C., the loss of heat by radiation from even the single perforated reflector-type vacuum jacket is appreciable; and the use of a double perforated reflector becomes desirable. By the use of the separate sleeve-type vacuum-jacket construction, it also becomes possible to insert a miniature fine resistance wire heater into the annular clearance space between outside of distilling tube proper and the inner tube of the vacuum jacket. Heat may then be supplied to this heater in sufficient quantity to compensate exactly for the residual heat loss through the perforations and through the reflector walls. A suitable column assembly is described below.

Experiments to Provide Differential Expansion of Vacuum Jackets. At this point in the investigation it became necessary to make some provision for the differential thermal expansion effect of the inner and outer tubes of the fractionating column already commented upon, which, at higher temperatures, invariably led to fracture through progressive bowing of the weaker inner tube. It is surprising how an apparently inappreciable elongation produces an inordinately large deflection. This is illustrated in Figure 15 based on computation from thermal expansion coefficients and actual experimentation. As a matter of fact, neither soft glass nor an all-Pyrex column or vacuum jacket will survive the temperature difference of 300° C. as shown in the figure.

In a search to conquer this difficulty, various devices were experimented with, including a bubble column in which an elastic corrugated glass bellows absorbed the differential expansion, and a metal-glass column in which a metal bellows was sealed to form a section of the inner or outer tube of the jacket. The only practical and entirely satisfactory construction was found to be one wherein the inner tube was made of transparent fused quartz, while the rest of the jacket was made of Pyrex. The quartz tube is attached to the Pyrex through specially well made graded joints. Fused quartz is known to have a negligible thermal expansion coefficient, while the Pyrex exterior of the column is not exposed to high temperatures and, therefore, the expansion of both the inner and outer tubes of the jacket is negligible. The practically complete elimination of deflection and of the resulting strains or breakage is shown graphically in Figure 15. The Pyrex vacuum-jacket columns shown by Leslie (*17*), Cooper (*8*), and Bush and Schwartz (*6*) could not possibly have survived to temperatures much higher than about 100° C. unless the heat insulation of the jacket was so poor that the temperature of the outer wall was not greatly different from the temperature of the inner wall.

Fused quartz, in addition to its negligible thermal expansion coefficient, has a very high melting point (above 1600° C.) and is much more resistant to deterioration at high temperatures than Pyrex or plain glass. It is therefore especially suitable for use in a high-temperature distilling column. Since it does not deteriorate at any temperatures within the recommended range, it does not give off sufficient gas to spoil the vacuum.

The most thorough precautions have to be taken for proper evacuation of such high-temperature columns, including thorough degasification of the vitreous and metal parts (using high-frequency high-voltage bombardment methods for the metal parts) and the use of very efficient getters to maintain the original high vacuum (better than 0.00001 mm.) throughout a reasonably long operating life. Sufficient tests of such

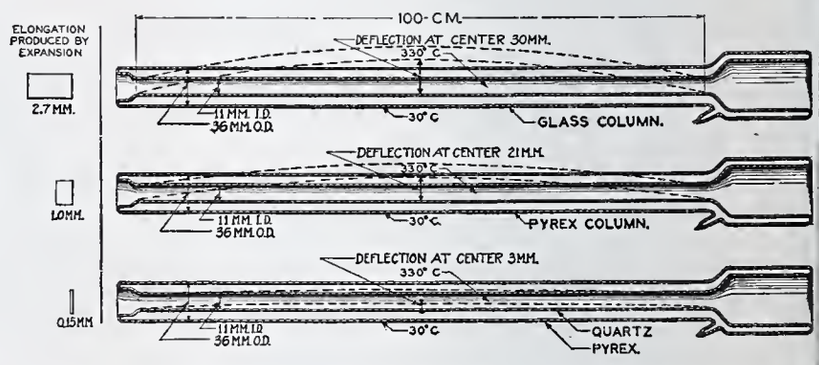

Figure 15. Differential Expansion of Vacuum-Jacket Columns at Higher Temperatures

columns have been made to prove that a high vacuum can be maintained indefinitely if the maximum operating interior temperature of about 350° C. is not exceeded. The dependability of the quartz-Pyrex construction is of a high order and breakages have practically not been experienced, even though the column was allowed to overheat to inside temperatures as high as 500° C.

Factor 8. General Design and Construction of Fractionating Column Assembly and Apparatus

The importance of this factor is paramount in that the design of the fractionating apparatus fixes factors 4, 5, 6, and 7. Conversely, the design of the apparatus is quite definitely outlined in its essentials by the requirement of highest (or lowest) ratings of these factors with due regard to their relative importance. All four factors mentioned apply to the frac

tionating column alone. However, the accessory apparatus for supplying heat to still, cooling to reflux, indicating or recording reflux temperature and amount of distillate, pressure control, etc., as discussed under factor 3, must be designed to correspond to the functioning characteristics and requirements of the fractionating column used. The sensitivity and accuracy inherent in the fractionating column will be lost unless the accessory apparatus is so designed as to take advantage of them.

The general design and operation of low-temperature fractionating apparatus are described in the first article of this series (*19*), and in Part IV, to follow. The high-temperature fractionating apparatus is described in Part III in this issue.

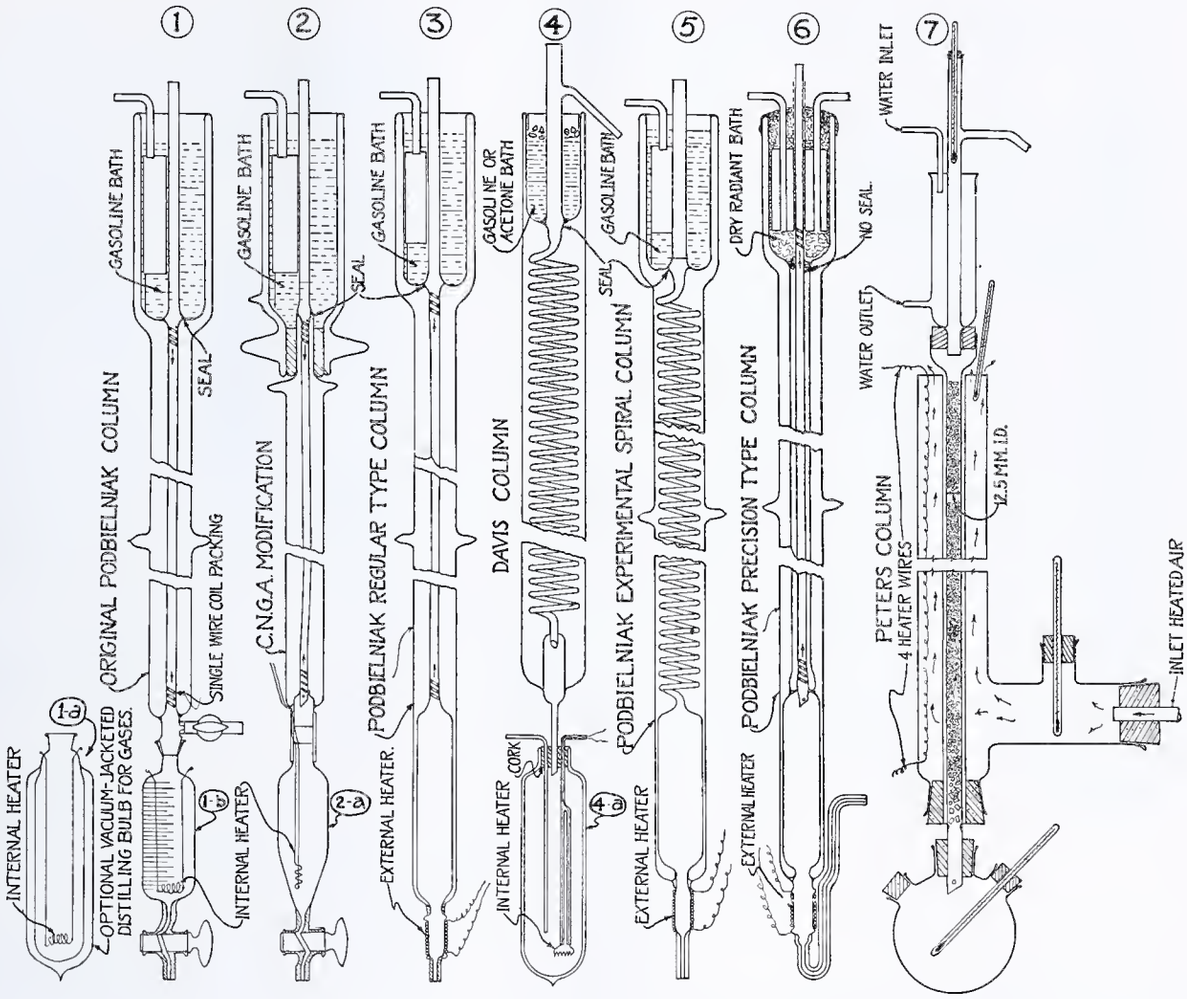

FIGURE 16. COMPARISON OF INSULATED COLUMNS 1 TO 7

COMPARISON OF FRACTIONATING COLUMNS PREVIOUSLY DESCRIBED. Figure 16 shows various columns previously described in the literature designed for high fractionating efficiency. These columns incorporate, with more or less modification, the distilling tube and packing elements shown in Figure 1 and the same general comments and criticisms apply as under factors 4 and 5. Columns 1 to 5, inclusive, and 7 have excess liquid hold-up in the reflux and this alone destroys their usefulness for most effective fractionation as discussed under factor 5. The spiral columns 4 and 5 have excess hold-up of liquid in the column tube proper, in proportion to maximum capacity, and cannot possibly be as effective as straight vertical unpacked tubes of same length and bore. Column 7 is packed with glass cylinders and suffers from the high hold-up and low capacity shown for glass cylinder packing in Figure 1. The Precision or semi-sleeve type of column is the best fractionator in this group from the standpoint of factors 4 and 5 ratings. The seal at the lower end of the fractionating section is objectionable from a practical standpoint but it does not affect the rating of factors 4 or 5, as in the case of a seal in or above the fractionating section.

PRACTICAL FEATURES. The expansion bellows separate reflux chamber of the C. N. G. A. modification (column 2) is especially objectionable on account of its fragility. In order to provide sufficient flexibility for use at internal liquid air temperatures, the bellows must be made of large outside diameter and with very thin walls. When it is considered that the atmosphere exerts a total pressure of about 150 lb. (10.33 kg. per sq. cm.) on the lateral walls of the bellows, the inherent high fragility of this type of construction is evident.

Columns 2 and 4 as described have very large reflux chamber capacity, resulting in abnormally long time of distillation even for easy separations, as the heat capacity of the large amount of reflux bath liquid and of the glass walls is very high, necessitating both undue consumption of refrigerant and a large time lag in controlling reflux cooling. The upper and lower seals of columns 1 to 5, inclusive, and also the lower seal of column 6 have been found objectionable in actual use because of their mechanical and thermal fragility: For low-temperature work a certain amount of "bow" is originally introduced into the inner or distilling tubes of vacuum jackets. The effect of lowering internal temperature is to cause the inner tube to straighten partially because of differential contraction. This straightening introduces a certain amount of tensile stress in the inner tubes, frequently resulting in fracture of the inherently weak triple-wall seal junctions. For high-temperature work the inner tube is made originally straight and tends to increase in length or to bow, thus putting a compression stress on the end seals, with similar liability to fracture in the case of the triple-wall junction type of seal. A still further objection to the integral distilling tube and the vacuum-jacket type columns is the fact that the condensing tube is inflexible and fragile, and its fracture necessarily requires rebuilding or replacement of the entire fractionating columns.

STANDARD PRECISION FRACTIONATING COLUMNS. In order to eliminate these various objections, columns were developed for both low- and high-temperature work as illustrated in Figure 17. Column assembly 8 is designed for low-temperature and column assembly 9 for high-temperature fractionations. Both are of the separate sleeve-type vacuum-jacket construction and have the radiant or dry reflux cooling vessel, similar to the one previously described (*19*) but with certain modifications. Either the low- or the high-temperature

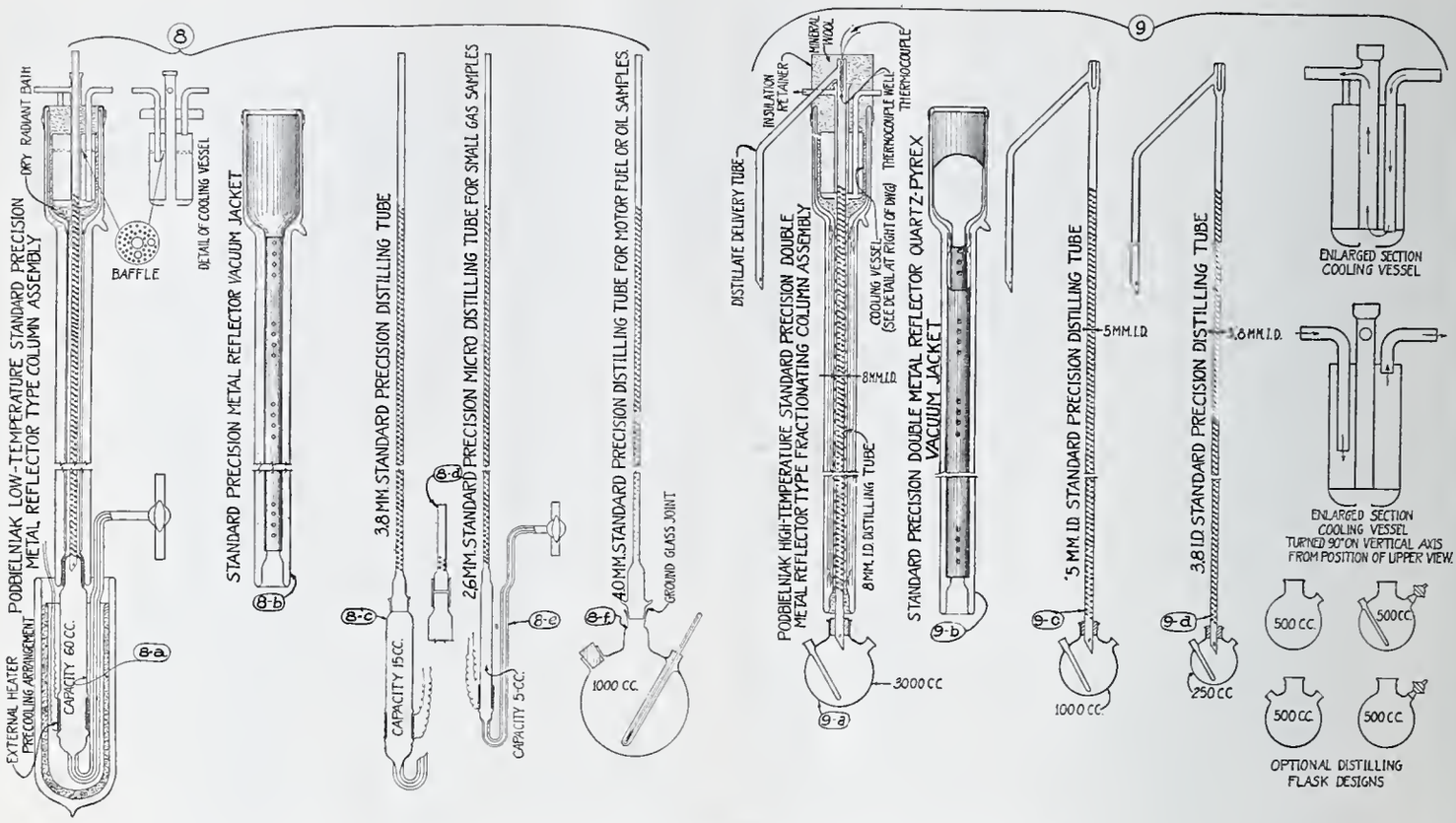

FIGURE 17. STANDARD PRECISION FRACTIONATING COLUMNS

8. Metal reflector low-temperature assembly
9. Metal reflector high-temperature assembly

vacuum jacket may be used with a variety of interchangeable separate distilling tubes and flasks. The vacuum-jacket construction includes only smooth seals, while the distilling tube is completely free from bulky seals or other discontinuities. The distilling tubes are similar to tubes *A*, *B*, *E*, *G*, and *H* as described under Figure 1, and range from 2.6 mm. to about 4.5 mm. in the case of the low-temperature column and from 2.6 mm. to 8.0 mm. in the case of the particular high-temperature column illustrated in Figure 17. A larger high-temperature column has also been developed to accommodate distilling tubes from 8.0 mm. or less up to about 15 mm. inside diameter and will be described in detail in a later paper of this series. The packings used are the single-wire coil up to about 6 mm. inside diameter and a double-wire coil, a flat-strip coil, or other spiral continuous type of packing up to the largest sizes.

In many cases, it is advisable to subject a highly complex sample or one with only a very small percentage of the component to be separated or determined analytically, to a preliminary fractionation in a large-capacity column and to complete the fractionation in a smaller-capacity column. With the separate vacuum-jacket distilling tube combination, it is only necessary to change distilling tubes to secure the desired large or small capacity, while this paper presents the essential data on sharpness of separation and capacities which may be secured with straight vertical tubes, packed with any of the packings tested.

DIFFERENCES OF LOW- AND HIGH-TEMPERATURE COLUMNS. While basically similar, the low- and high-temperature columns 8 and 9 differ in many important respects in accommodation to their respective temperature and sample size ranges. The low-temperature column has only a single perforated reflector in the vacuum space of the vacuum jacket, whereas the high-temperature column has a double reflector plus a compensatory miniature resistance wire heater inside the jacket inner tube. The low-temperature column depends on initial bowing of the Pyrex inner tube to compensate for differential contraction; whereas the high-temperature column necessarily includes a quartz inner tube (with rest of jacket of Pyrex) to withstand its extreme temperature range. The high-temperature jacket accommodates larger distilling tubes than the low-temperature, inasmuch as larger samples are more frequently required in high-temperature work than in low-temperature analysis.

The dry reflux cooling arrangement illustrated in Figure 17 has been found entirely satisfactory and unqualifiedly superior to any type of gasoline or other liquid bath, because of its low heat capacity, superior heat transfer, inappreciable time lag in response to cooling, versatility, and complete freedom from tendency of liquid to freeze or to explode, over the temperature range from the boiling point of liquid air to about 300° C. The low-temperature cooling vessel is provided with a soldered-on cap and packing gland to exclude atmospheric moisture which might otherwise condense and freeze in the reflux chamber. The high-temperature cooling vessel is similar in general construction but has no cap and is brazed to withstand the higher temperatures. The arrangement of optional direct contact and indirect cooling conduits has already been described (*19*).

The high-temperature cooling vessel may be used alternatively with liquid air, liquid carbon dioxide, brine, water, or compressed air as refrigerant. The heat capacity of this type of cooling vessel can be made less than that possible with any practicable type of gasoline or liquid bath.

Fenske, Quiggle, and Tongberg (*14*) describe very tall metal fractionating columns, which, by all the criteria set forth in this series of articles and by inspection of the actual analytical data presented, are far superior to all other precise fractionating columns described in the literature (with the exception of the preferred vacuum-jacket columns described in this paper). These columns are intended for research work on Pennsylvania petroleums. The smaller column is of especial interest. It is made of (1.9-cm.) 0.75-inch inside diameter brass pipe 52 ft. (15.84 meters) long lagged with thick layers of 85 per cent magnesia, and also provided with sectional electric resistance wire

heaters, controlled by the use of differential thermocouples. This method of thermal insulation seems to be the logical one for metal columns of great height, and the column deserves a very good rating in factor 7. The importance of minimizing hold-up of liquid and vapor in the column, and especially in the condensing section as discussed under factors 4 and 5, seems to be fully appreciated and the column designed accordingly. Reflux temperatures are measured with a fine wire thermocouple and a potentiometer as with the present apparatus. The wire "helices" described are equivalent to sections of the wire coil packing as described by the author (*19*) and should be superior to jack chains and Lessing rings, although not as efficient as a truly continuous helical packing. Actually, the separations secured for definite total distillation times and reflux ratios are much superior to those obtained in the other equipment reviewed. The substantial agreement of Fenske and his associates with the author, as regards the fundamentals of highly effective fractionating column design, is very gratifying. However, the Standard Precision high-temperature fractionating columns (Figure 17) are believed to be more highly developed in thermal insulation and especially in the helical continuous type of packing used. The fractional distillation curves shown in Figures 3 to 13, Part III, are superior to those presented by Fenske and associates although the latter used a tall column as described and as much as 5 days per distillation.

The vacuum-jacket and distilling tube combinations presented in Figure 17 represent the final development of this investigation. Essentially the same type of column, with only such structural modifications as the double *vs.* single reflector and the use of quartz-Pyrex construction for higher temperatures, gives at the same time the most precise fractionation and the most practical results that have yet been described in the literature over the enormous reflux temperature range of −190° C. (this temperature is based on the use of liquid air, but can be lowered if lower-boiling refrigerants can be obtained) up to 300° C. By the use of vacuum distillation, hydrocarbons with boiling points as high as 500° C. can be distilled. Either gaseous or liquid samples ranging from about 0.3 cc. (liquid equivalent) when using the micro 2.6-mm. tube, up to 20,000 cc. in size when using a 15-mm. tube, can be expeditiously distilled in not very many hours to give extremely precise separation of close boiling components as illustrated in Figures 4 to 13 in Part III.

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* * * * *

III. Apparatus for Precise High-Temperature Fractionation of Complex Liquid Mixtures

A description and typical results are presented of a precise laboratory fractionating apparatus suitable for distilling complex liquid mixtures, such as motor fuels, lubricating oils, petroleum crudes, commercial solvents, etc., at reflux temperatures ranging from −190° to 300° C. and at distillation pressures ranging from 1000 to 1 mm. mercury absolute. Novel means are described for reflux temperature measurement, collection and measurement of distillate, changing of receivers in vacuum distillation, and vacuum control, possessing greater precision and convenience than the usual apparatus. Distillations may be made in only a few hours, showing materially better separation of close-boiling components than those made in other apparatus previously described in the literature. One apparatus with only a change of distilling tubes within a sleeve-type vacuum jacket may be used for distillation of liquid samples ranging from a few to 3000 cc. in size (20,000 cc. or more with a slightly modified apparatus of the same general design).

Part II of this series (*6*) described the Standard Precision type of high-temperature fractionating column and gave certain essential requirements of the complete fractionating apparatus assembly and analytical procedure. The present paper describes a complete fractionating unit, incorporating the Standard Precision column assembly suitable for precise laboratory fractionation of complex liquid mixtures at reflux temperatures ranging from −190° to 300° C. and at distillation pressures ranging from 1000 to 1 mm. mercury absolute. The apparatus is based on the principles discussed in Part II and possesses many new features not previously described in connection with laboratory fractionating apparatus.

The general appearance of the complete apparatus is shown in Figure 1. It is designed compactly and for greatest ease and convenience in operation. All rheostat control knobs and switches are mounted on a single switchboard panel. Reflux cooling is regulated by turning a fine needle valve controlling compressed air supply. For reflux temperature measurement a portable millivoltmeter or potentiometer

is used, conveniently disposed on the apparatus table. Distillate volumes are read from long, finely graduated burets located at eye level, instead of the usual short graduates. Changing of distillate-receiving burets during either atmospheric or vacuum distillation is accomplished by merely shifting the receiver change-block slide. In vacuum distillation it is necessary to set the vacuum control for the desired pressure as described and no further attention is thereafter needed.

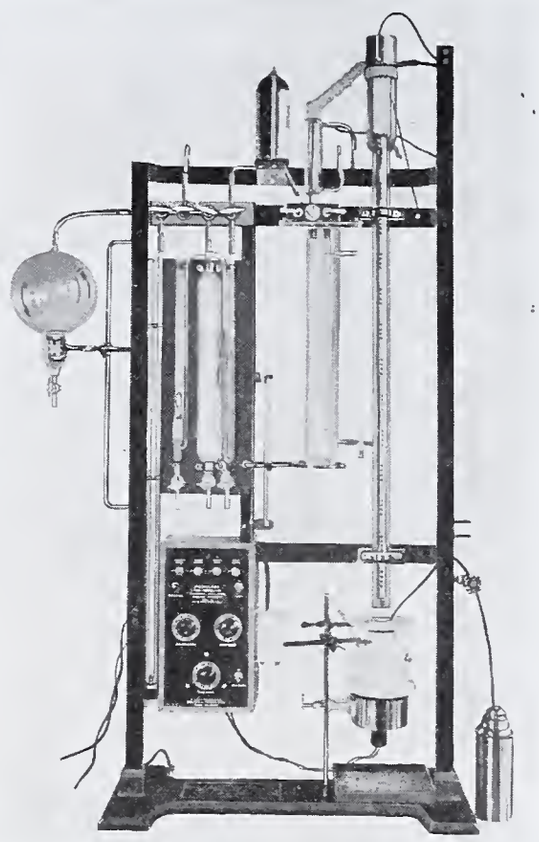

Figure 1. Standard Precision High-Temperature Fractionating Apparatus

Fractionating Column Assembly

Figures 1 and 2 illustrate the Standard Precision high-temperature fractionating column assembly incorporated in the complete fractionating unit. The vacuum jacket is 11 mm. minimum inside diameter and will accommodate distilling tubes ranging from 2.6 to 8 mm. inside diameter, corresponding to convenient sample sizes of about 5 to 3000 cc., respectively. Although a small amount of air at atmospheric pressure is present in the annular clearance between the outside wall of the distilling tube and the inside wall of the vacuum jacket, this has no appreciable effect on either the efficiency of the insulation or the thermal gradient in the distilling tube (*6*). (A somewhat modified vacuum jacket of the same general type but designed to accommodate tubes as large as 16 mm. inside diameter, of about 20,000 cc. convenient sample capacity, will be described in a later paper.)

The distilling flask varies from 50 to 3000 cc. in capacity and is provided with at least a single outlet and a thermometer well. The joint between distilling flask and tube is made by means of a high-grade very well fitted cork, sealed with LePage's glue. Ground-glass joints have not been found satisfactory for high-temperature work. The still heater is preferably of the radiant type such as the Cenco Hotcone heater, and is regulated by a rheostat as shown.

Measurement of Reflux Temperature

In order to utilize fully the sharp fractionation characteristics of the Standard Precision type columns, the reflux temperature must be measured with high accuracy, especially in the higher boiling point ranges. The use of a thermometer in precise fractional distillations is highly unsatisfactory (*1*) because of errors due to conduction of heat along stem, radiation and stem exposure, short range, and, what is very important, bulkiness leading to undesirable high hold-up of liquid (*6*).

The present apparatus therefore includes a single-junction fine-wire thermocouple (preferably iron-constantan on account of its more uniform and reproducible e. m. f. curve) and e. m. f. indicator, the latter being either a high-grade millivoltmeter (such as the Engelhard portable millivoltmeter) or a portable potentiometer instrument (such as the Brown portable potentiometer). A millivoltmeter has the advantage of direct reading; however, a sensitive potentiometer is preferred in the case of distilling higher molecular weight compounds of very close boiling points, where the exact determination of reflux temperatures is very important.

The direct determination of reflux temperature has been generally criticized by Bruun (*1*) in favor of using the Cottrell boiling point apparatus. However, the latter introduces a hold-up of distillate which would completely destroy the sharpness of separation obtainable with the fractionating equipment as described in this article. The reëntrant thermocouple well, thermocouple and potentiometer system of direct reflux temperature measurement (Figure 2) were tested against (1) boiling points of a variety of pure liquids such as carbon bisulfide, ether, acetone, benzene, toluene, aniline, nitrobenzene, etc., actually distilled in the column, and (2) various synthetic mixtures of these chemicals to cover large boiling point ranges. The distillation rate and reflux ratio were varied during these tests without appreciable effect on the thermocouple readings until a distillation rate as low as about 0.4 cc. per minute was reached. (In a closed air-free system as used in low-temperature fractionations (*5*), correct temperature readings are secured even with zero distillate rate.) Below this rate the reflux temperature readings began to fall off. Inasmuch as this low rate is exceedingly low, it must be concluded that the present reflux temperature measuring system gives highly reliable and accurate indications of the true boiling point of the very small portion of the distillate passing the thermocouple. However, the use of a well-insulated reflux chamber and of continuous or semi-continuous rather than violent occasional cooling is essential in order to obtain the above results.

Collection and Measurement of Distillate

Distillate Receivers. The distillate is collected in long (48-cm.) finely graduated special test tubes with upper stems of proper dimensions to fit the nipples of the receiver change block to be described. It has been found convenient to make these tubes in 10, 25, 50, and 100 cc. capacities in order to secure desired accuracy of measurement on samples of varying size. A tall cylindrical water jar with provisions for flow of water is used as a constant-temperature bath.

Receiver Change Block. The usual devices for changing receivers during vacuum distillation have not been found suitable for use with the present apparatus. Stopcock devices are inherently unsatisfactory because of lubricant troubles and undue complication. The usual desiccator type (*4*, *8*) of receiver-changing apparatus is not suitable for long burets to be maintained at constant temperature; also, the large volume of this type of apparatus causes large errors due to vaporization of distillate and to blending of the fractions through interdiffusion of vapors. Accordingly a

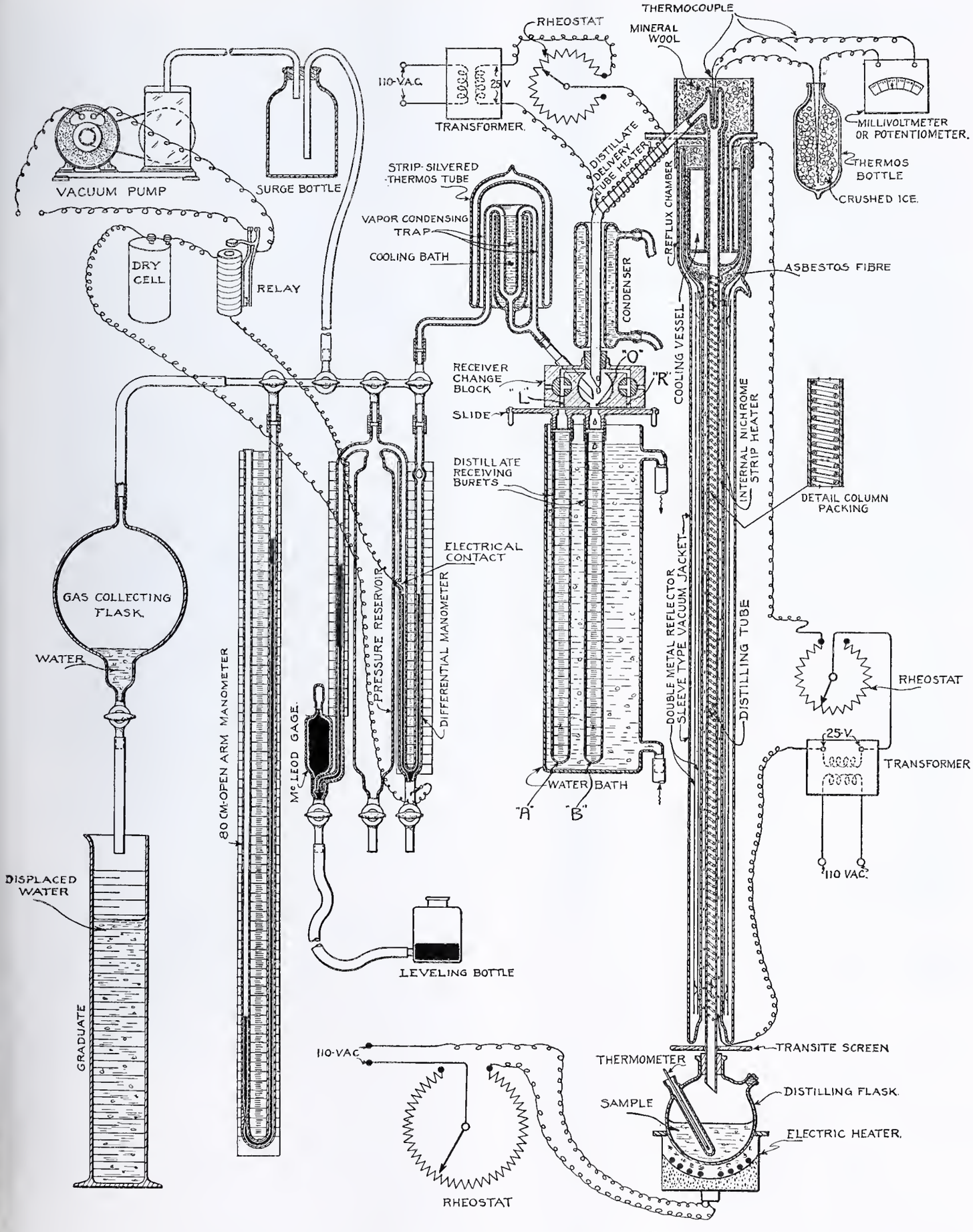

FIGURE 2. DIAGRAM OF STANDARD PRECISION HIGH-TEMPERATURE FRACTIONATING APPARATUS

receiver change block device was developed for this apparatus (Figures 1 and 2) which makes possible change from one receiver to another without the loss of a drop of distillate or cubic centimeter of vapor, and with no restrictions on the dimensions of the measuring graduates or burets.

A ground metal slide carries two metal nipples onto which are connected, through rubber tubing, the correspondingly shaped upper stems of the burets *A* and *B*. When buret *B* is to be changed, the metal slide is shifted to the right, thereby moving buret *B* under metal stopcock *R* and simultaneously moving buret *A* under the delivery tube *O* to receive distillate. Buret *A* should

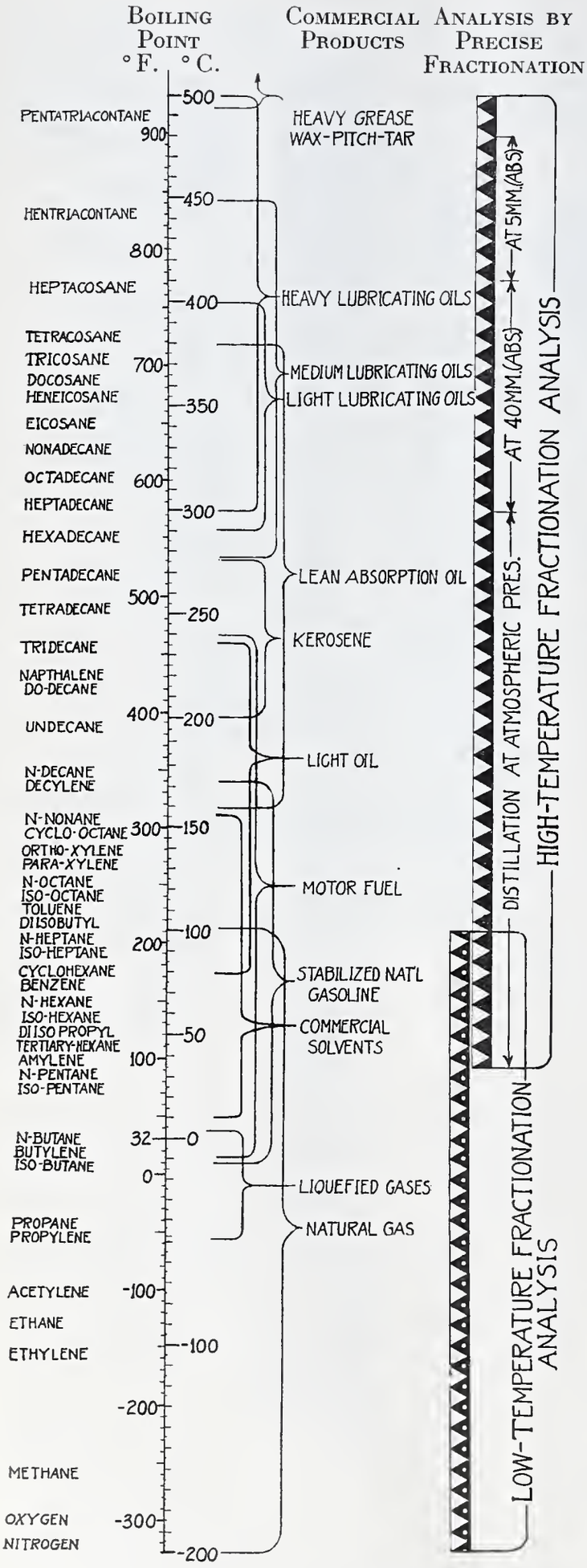

Figure 3. Diagram Illustrating Scope of Precise Fractionation

previously have been exhausted to column distillation pressure by properly turning the metal stopcock *L*. The vacuum in buret *B* is released through stopcock *R* to air and this buret may then be disconnected at leisure. Complete visibility is retained through the use of glass windows in the change block. An inclined return tube is provided to deliver continuously (and visibly) to the distillate receiving buret any condensate returned to the block by the vapor condensing trap. The slide is, of course, very well ground and lapped into the body of the change block and must be greased with a suitable lubricant to prevent leakage at even very low pressures. Bruun (*1*) mentions lubricants which are especially suitable for distillation of aliphatic hydrocarbons. However, fairly good results may be obtained with ordinary heavy oil or glycerol.

This device has been found convenient and satisfactory for its purpose. As many as several dozen carefully measured fractions may be taken from a single sample, without interfering with taking readings or plotting a complete fractional distillation curve, and without adding to the time or difficulty of the analysis. It is suitable for use over a wide range of pressures, 1000 mm. or higher (using springs to keep the slide against its seat) down to as low as 1 or 2 mm. absolute.

Collections of Condensable Vapors. In all distillations except in the closed system used in low-temperature fractionation analysis, there is a certain loss of the lower boiling components, due to vapors escaping condensation in the condenser and passing out to the atmosphere or to the vacuum pump in the case of vacuum distillations. In the case of vapors of substances normally liquid or with boiling points only slightly below room temperature (such as iso- or *n*-pentane), the use of a special vapor-condensing trap as illustrated in Figures 1 and 2 makes it possible to condense continuously practically all such condensable vapors and to return every drop of condensate formed within it to the distillate-receiving buret with the least practicable lag or hold-up of liquid. The usual method of collecting all condensate in a bulb-type trap merely measures the total amount of vapors escaping the condenser during distillation but does not give any data for correcting the distillation curve. This latter is done automatically with the present arrangement. The choice of cooling mixture in the trap depends on the nature of the vapors and may be liquid air, carbon dioxide, acetone, or crushed ice. An inverted thermos tube (strip-silvered for visibility) is placed over the trap to supply almost perfect thermal insulation as long as desired.

Collection, Measurement, and Analysis of Noncondensable Vapors. The use of the vapor-condensing trap will not of course suffice to retain in the distillate air as originally present in the distilling system or permanent gases with boiling points more than about 10° or 15° C. below room temperature. Accordingly, an external 3000-cc. gas-collecting flask is used for collection and measurement of the air-vapor mixture leaving the vapor-condensing trap. It is of special usefulness in the very first part of atmospheric distillations, when all the air in the distilling system is expelled together with a certain amount of gases from the sample, and when it is required to correct for the gases thus escaping condensation.

When the volume of noncondensable vapors liberated from the sample is very large, as in the case of natural gasoline or high-gravity crude oil, it may be necessary to replace the 3000-cc. flask with a calibrated 3-gallon (11.3 liter) or 5-gallon (18.9-liter) bottle or even a wet test meter. The reflux may be cooled with liquid carbon dioxide or even with liquid air to secure any desired degree of separation of the more volatile from the less volatile hydrocarbons. In this way, samples containing components with boiling points ranging all the way from that of methane (−161.4° C.) up to those of lubricating oil fractions (500° C. and higher as corrected from results of vacuum distillation) may be distilled completely, without distillation loss.

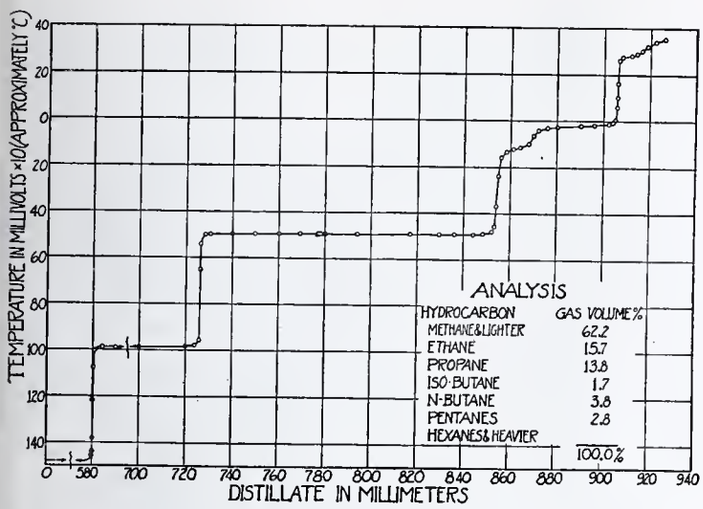

FIGURE 4. LOW-TEMPERATURE DISTILLATION OF NATURAL GAS

The noncondensable gases liberated during distillation and collected in either the 3000-cc. special flask or in the larger-capacity bottles may be analyzed either by the conventional absorption and slow combustion tests or by the low-temperature fractional-distillation analysis apparatus and method described in Parts I (*5*) and IV of this series. By this procedure, using the two precise fractionating apparatus developed by the author for low- and high-temperature distillation range, it is possible to secure practically complete fractionation of any distillable mixture of even the most extreme boiling point range by a relatively simple and highly accurate procedure. Figure 5 illustrates the complete distillation of a typical motor fuel by this combined procedure.

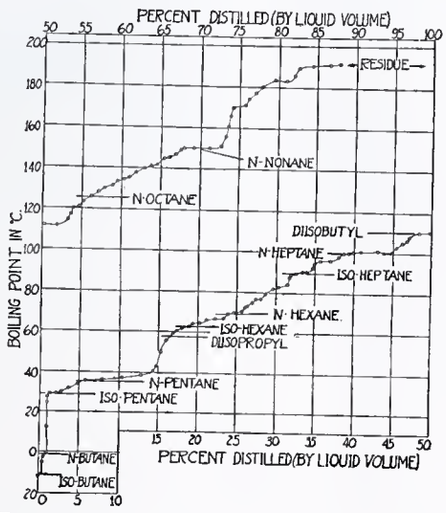

FIGURE 5. COMBINED LOW- AND HIGH-TEMPERATURE DISTILLATION OF TYPICAL MOTOR FUEL

VACUUM CONTROL

Inasmuch as almost all organic liquid mixtures begin to decompose thermally at prolonged heating above about 350° C., it is inadvisable to permit the temperature in the distilling flask to go higher than that, especially since higher temperatures might tend to deteriorate the vacuum in the vacuum jacket through liberation of adsorbed or chemically combined gases from interior glass walls. However, a temperature of 350° C. in the still usually corresponds to about 300° C. in the reflux. In order, therefore, to distil components of higher boiling point than about 300° C., the distillation must be conducted at lower than atmospheric pressures.

The usual closed-arm manometer type of vacuum-control apparatus as described by Dean (*2*) and others is open to many objections. To overcome these objections, a vacuum-control apparatus, based on the null-point principle as used in temperature-recording potentiometers, has been developed (Figure 2).

In preparing for vacuum distillation, the standard pressure reservoir is evacuated with the vacuum pump until its pressure as indicated either on the long open-arm manometer or on the McLeod gage is exactly equal to the desired distillation pressure. The standard pressure reservoir and the McLeod gage are then shut off from the rest of the system by closing the intervening stopcocks. The distilling column system is evacuated approximately to the desired distillation pressure as indicated on the open-arm manometer, at which stage the stopcock nearest the receiver change block is turned to connect the distilling system to the right arm of the differential manometer. Whenever the distillation pressure exceeds the pressure in the standard pressure reservoir, electrical contact is made by the mercury on the left side of the manometer, a low-voltage circuit, including a large-capacity condenser and a relay, is completed, and the relay in turn actuates the vacuum pump. The distillation pressure is lowered by the action of the vacuum pump until it becomes equal to the desired pressure, when the electrical contact in the differential manometer is broken until the next minute increase in distillation pressure. In this way the distillation pressure is maintained constant to less than 0.1 mm. of mercury. Any leak in the standard pressure reservoir would be indicated immediately on the McLeod gage which is connected to it at all times. The make-and-break electric contact occurs on the air side of the differential manometer and there can never be any risk of igniting explosive vapors resulting from distillation. The bore of the differential manometer is made over 9 mm. to avoid sticking of mercury, as recommended by Weaver and Ledig (*10*). The whole apparatus can be drained of mercury at any time, cleaned, and refilled with medium pure mercury, in a very simple manner.

Any dependable vacuum pump which will produce the desired degree of vaccum may be used, although the Cenco Hyvac pump has been found especially suitable. In the case of laboratories which have a line affording a sufficient vacuum, the vacuum pump may be replaced by a compact electromagnet valve.

By the use of vacuum distillation, components of boiling points up to about 500° C. may be fractionally distilled. Usually, atmospheric distillation is followed by distillation at 40 mm. absolute as used by Dean et al. (*2*), followed by a distillation at 5 or 2 mm. absolute if required. Naturally, at these low pressures the capacity of the distilling tube decreases considerably, and a proportionately larger diameter

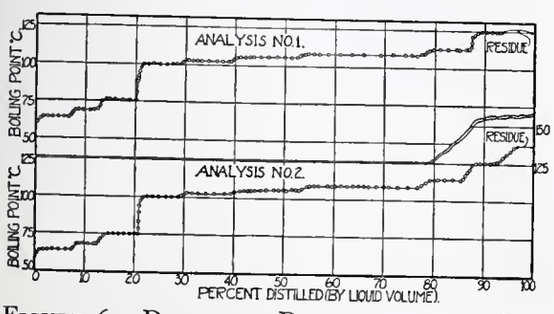

FIGURE 6. DUPLICATE DISTILLATIONS OF COMMERCIAL LACQUER THINNER

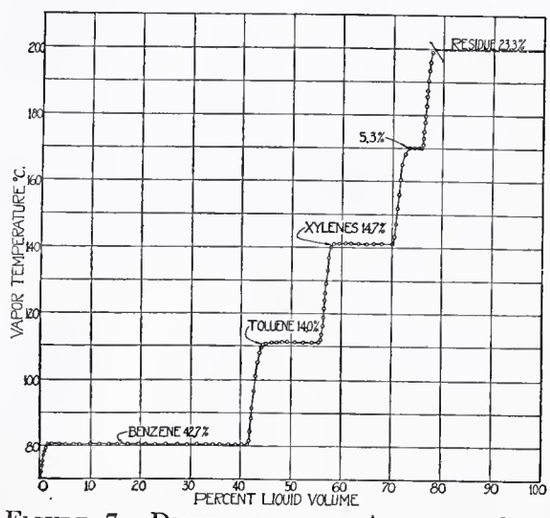

FIGURE 7. DISTILLATION OF AROMATIC CONDENSATE FROM CRACKED NATURAL GAS

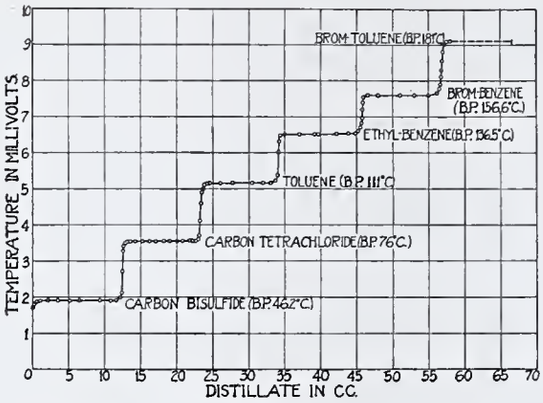

FIGURE 8. DISTILLATION OF SYNTHETIC MIXTURE

distilling tube is used for vacuum than for atmospheric distillations. Correction of boiling points to atmospheric is made by the use of a simple semi-logarithmic plot of vapor pressures of the principal hydrocarbons or other compounds being distilled (*7*).

The vacuum-control assembly and method of boiling point correction have been found highly satisfactory in every way. Curves shown in Figures 9, 10, 11, and 12 were run using this vacuum control device and correcting the reflux temperatures to atmospheric. The curves are practically continuous, showing the precision of both the fractionating column and means of reflux measurement, and the vacuum-control mechanism and boiling point correction.

ANALYTICAL PROCEDURE

Distillation with the apparatus consists essentially of regulating the supply of heat to still and reflux to cooling to obtain sharpest possible fractionation of sample within the time available and of recording and plotting frequent simultaneous readings of reflux temperature and amount of distillate to be used in plotting the fractional distillation curve.

Contrary to most accepted practice, the column is regulated so that the packing is barely wet (*6*). The reflux ratio (as determined by a comparison of number of drops falling from the bottom end of the distilling tube and from the end of the distillate delivery tube, respectively) is varied as the apparent difficulty of separation. The distillation rate is not allowed to decrease below about 0.4 cc. per minute, as otherwise the reflux temperatures would not be representative. Because of the efficiency of the fractionating column, it is not usually necessary to use average reflux ratios (averaged over the total time of distillation) much higher than about 6 to 1 in order to obtain sharp fractionation.

The distillate delivery tube heater is used at temperatures above about 150° C. and for low distillation rates in order to prevent backward diffusion of air to the thermocouple. The jacket heater need not be used until a temperature of about 200° C. is reached in the reflux when it is gradually cut in, using the regulating rheostat, to offset the tendency of the column to flood due to heat leakage. Flooding due to heat leakage usually manifests itself at the bottom of the column packing. If, however, the column tends to flood at the top, this would mean that either too much heat is applied at the still or the distilling tube is too small in diameter for the attempted distillate rate at the particular distillation pressure used.

The time of distillation will of course vary greatly, depending on the size and nature of the sample distilling tube used, distillation range, accuracy desired, etc., and will range from one hour to several hours. The size of sample may range from 5 cc. of liquid, using the 2.6-mm. inside diameter distilling tube, to as much as 3000 cc. or more using the 8-mm. inside diameter tube. Similar apparatus but of larger capacities up to 20,000 cc. will be described in a later paper of this series. Part II (*6*) gives complete data on distilling capacities of tubes of these and intermediate diameters. The range of distillation is from −190° to 300° C. reflux temperature and from atmospheric down to a few millimeters of mercury absolute distillation pressure. Distillation at pressures below 1 mm. of mercury is not usually practicable because of the limitations of any packed fractionating column for such low pressures.

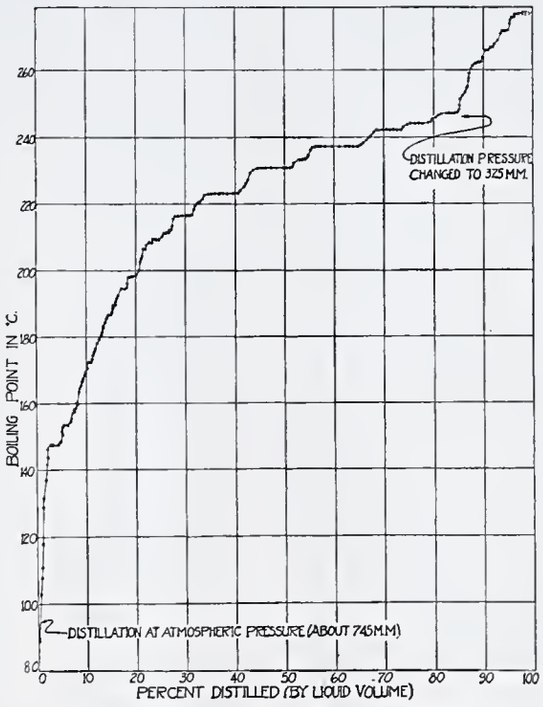

FIGURE 9. DISTILLATION OF KEROSENE

GRAPHICAL PRESENTATION OF TYPICAL RESULTS

Figures 3 to 13 present graphically the distillation temperature range covered by the combination of the low-temperature fractionating apparatus as described in Parts I (*5*), II (*6*), and IV and the high-temperature fractionating apparatus described in the present paper; and fractional distillation curves for typical commercially important products covered by this distillation range.

Figure 3 shows the representative hydrocarbons naturally occurring in petroleum and other commercially important complex mixtures, arranged according to their boiling points adjacent to a vertical temperature scale.[3] The various products, such as liquefied petroleum gases, motor fuels, absorption oils, light oils, commercial solvents, lubricating oils, etc., are referred to their component hydrocarbons by means of brackets. The scope of high- and low-temperature fractional-distillation analysis is indicated by the heavy brackets composed of dark triangles. The apices of the triangles are 10° C. (18° F.) apart to

[3] Hydrocarbons represented on the scale as having boiling points considerably above 300° C. (572° F.) are subject to decomposition upon prolonged exposure to temperatures above 300° C., and it has therefore been

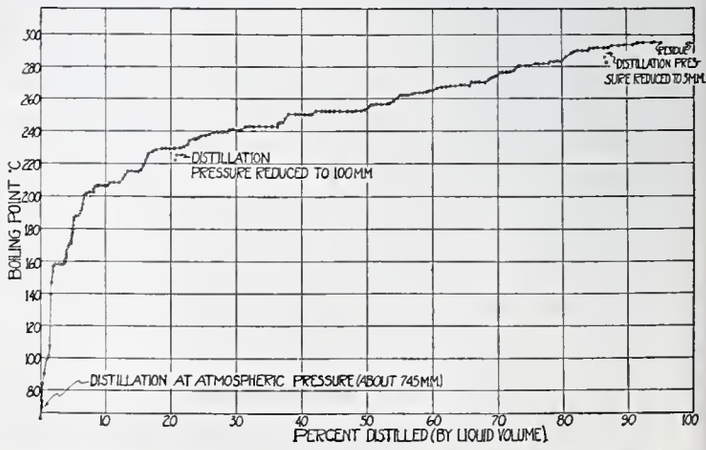

FIGURE 10. DISTILLATION OF STRIPPED ABSORPTION OIL

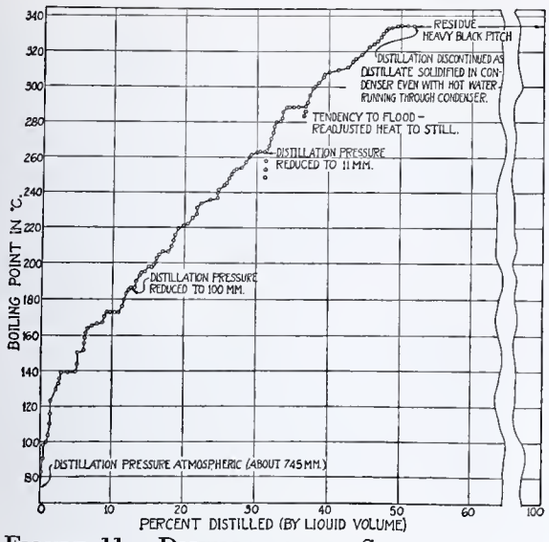

FIGURE 11. DISTILLATION OF SETTLINGS FROM CRUDE PETROLEUM STORAGE TANK

indicate that the fractionating or resolving power is sufficient to separate compounds boiling about that many degrees apart. Under favorable conditions the high-temperature apparatus will distinguish components boiling as little as 2.0° C. (3.6° F.) apart.

Figures 4 to 13, inclusive, are actual fractional-distillation curves obtained with the apparatus described on typical commercial samples of petroleum products, lacquer thinner, synthetic mixture, etc. Distinct plateaus are obtained even in the region of compounds with twelve or more carbon atoms to the molecule. Figure 6, showing duplicate distillations of a commercial lacquer thinner, illustrates the extremely close fractionation of components and the very close check secured. Figure 8 is the curve for a synthetic equi-percentage mixture of components, showing the practically perfect separation obtained. Figure 9,

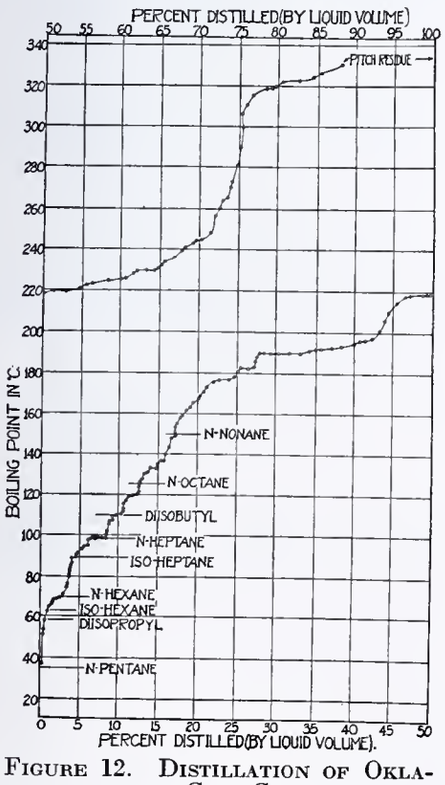

FIGURE 12. DISTILLATION OF OKLAHOMA CITY CRUDE

for a sample of commercial kerosene, shows a wealth of well-defined plateaus, which have been found to recur consistently at the same temperatures and in somewhat similar percentages in all other samples of petroleum products, as in Figures 10, 11, and 12. It will be noted that approximately 33 per cent of this kerosene boils below 425° F. (218° C.). The change of distillation pressure from atmospheric to 37.5 mm. does not introduce any material discontinuity in the curve, proving that the sharpness of separation of the fractionating column and the precision of the entire apparatus are of a high order. Figure 10 is a curve for a sample of stripped absorption oil used in natural gasoline manufacture. Approximately 15 per cent of this sample boils below 425° F. (218° C.), showing very poor stripping of the lighter hydrocarbons. Figure 11 is a distillation of a solid waxlike sample of settlings from a crude-petroleum storage tank. Although run at various distillation pressures, the corrected temperatures form a smooth and continuous curve. Surprisingly, almost 20 per cent of this material boils below 425° F. (218° C.). A residue of almost 50 per cent consisted of very heavy black pitch, which could scarcely be poured even at the highest still temperature. Figure 12 is a typical Oklahoma City crude showing peculiar characteristics in the upper temperature region and only 10 per cent of pitchlike residue. Figure 13 is a vacuum distillation of a medium heavy, S. A. E. 20 lubricating oil.

When compounds or fractions to be determined separately cannot be analyzed satisfactorily by precise fractionation because of small difference in boiling points, formation of constant-

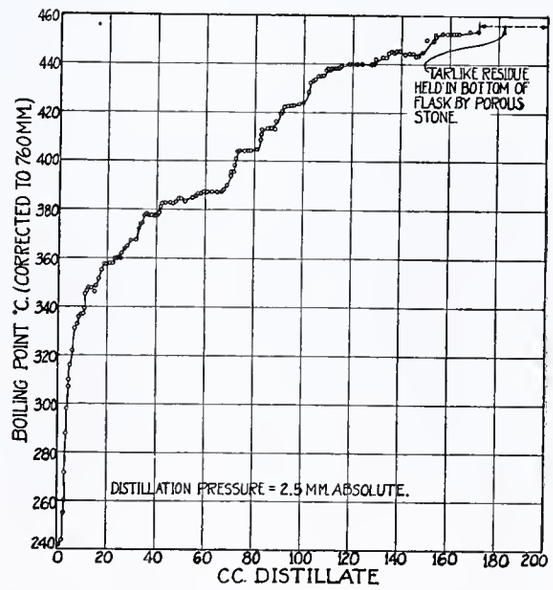

FIGURE 13. VACUUM DISTILLATION OF LUBRICATING OIL

boiling mixtures, or other reasons, or when it is desired to identify distillate fractions to determine their commercially important properties, supplementary tests such as the following must be made on the fractions.

Specific gravity or density
Refractive index
Viscosity
Molecular weight
Behavior with sulfuric acid
Flash and burning points
Carbon residue
Antiknock value
Halogen addition number
Aniline-point method
Redistillation at different pressures or in combination with additional components aiding separation
Selective solubility in special solvents
Freezing point
Optical activity
Selective crystallization and study of crystals

It will, of course, depend entirely on the purpose for which the test is made whether supplementary tests on fractions will be desired and which tests should be made (*9*). Ordinarily the precise fractional-distillation curve with specific gravity tests on selected fractions furnishes practically all the information needed.

Almost all these distillations were made as part of the routine of an analytical laboratory, and the time of distillation ranged from about 2 to 4 hours for the atmospheric distillations up to about 6 and 7 hours for distillations shown in Figures 11 and 13 which required one or two stages of vacuum distillation besides atmospheric. However, the results secured seem to be far superior in distillation capacity and sharpness of separation to those obtained by previous investigators.

necessary to obtain their standard boiling points by converting from boiling points taken at low pressures, through the use of suitable boiling point correction charts. Such corrected boiling points are by no means fictional, as it is well known that even very high molecular weight hydrocarbons can be heated without decomposition to temperatures normally resulting in extensive decomposition, provided the time of exposure to the high temperature is made sufficiently small.

The numerous plateaus shown in the case of petroleum products are extremely interesting. Petroleum is definitely broken up into comparatively simple fractions with distinctive boiling points (and percentages in the case of similar products) which consistently recur for a wide variety of petroleum products. The further study of these fractions to determine whether they are pure hydrocarbons, constant-boiling mixtures, or merely compounds of almost identical boiling point is highly interesting but not absolutely necessary to prove the extreme sharpness of separation secured; the latter is also evident from distillations of close-boiling synthetic mixtures and of more easily identified components such as the lacquer thinners (Figure 6) and from hundreds of distillation analyses of all types of samples made in this laboratory with this general type of apparatus in the last three years. Such efficient primary separation of the constant or practically constant-boiling components of petroleum or any other complex mixtures enormously simplifies the task of resolving these constant-boiling components into their individual compounds by the use of supplementary methods (*3*, *9*). Results of detailed study of some of the more distinctive plateaus secured above decane will be presented in a later paper.

Applications of Apparatus

The apparatus described in this paper is believed suitable for both research and routine industrial analytical work. Its high fractionating effectiveness and precision of reflux temperature and distillate measurement should make it extremely useful in the investigation of composition of complex mixtures, in accurate analysis, and in the preparation of fairly large quantities (up to several liters or more) of difficultly separable pure compounds, in reasonable time. It may also be used for the purification by fractionation of small quantities of compounds such as the individual isomers of heptane or octane or other organic compounds, which are required to be of a very high purity not obtainable by other purifying means, because of the presence of other chemically similar components. Incidentally, the use of the micro 2.6-mm. packed tube permits the fractionation of liquid samples only a few cubic centimeters in size.

However, the apparatus is also especially suitable, because of its reasonable time requirement, ease of operation, compactness, and other advantages, for the routine industrial analysis of a great variety of commercially important complex mixtures, such as motor fuels, commercial solvents, absorption oils, lubricating oils, petroleum crudes, liquid organic chemicals, etc. Such precise fractionation analyses have a unique field of usefulness, not possible with apparatus of lesser fractionating effectiveness, in testing manufacturing equipment and plants by the material balance method, or for the actual design of new equipments and plants from such fundamental analyses of the raw materials. This is especially true of the petroleum industry, where the lack of suitable analytical methods has been a serious handicap in developmental work.

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Combustion Train for the Determination of Total Carbon in Soils

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The method of determining total carbon in soils by the direct combustion of the organic matter in a current of carbon dioxide–free oxygen has been shown by Salter (*2*) to be not only satisfactory but rapid. This is especially true if ascarite is used as the absorbent for the carbon dioxide. Salter modified the procedure described by Fleming (*1*), which is used in the iron and steel industry. Fleming points out that the principle is not new and that the rate of oxygen current and combustion for iron and steel is limited by the efficiency of the apparatus used to absorb the evolved carbon dioxide. Winters and Smith (*3*) have reported data showing advisability of the use of 0.25 gram of manganese dioxide per 2 grams of sample charge in order to obtain perfect combustion and results comparable to those obtained with the wet combustion method.

The combustion train here described is a modification of those described by Salter (*2*) and Fleming (*1*). Special attention is called to several points in the assembly. The oxygen from the cylinder is let into the pressure system consisting of a rubber basketball bladder *A* and two 5-pint (2.37-liter) bottles, *B* and *C*. The difference in the level of the two bottles, *B* and *C*, is adjusted to give an oxygen pressure of about 0.75 inch (1.9 cm.) of mercury in the pressure gage *D* during the combustion period. The scrubber *F* contains a 30 per cent solution of potassium hydroxide and the chloride tower *G* contains first ascarite and then granular calcium chloride, separated by a layer of glass wool. The mercury valve *H* serves as a check and as an oxygen-flow indicator.

The silica tube *I* contains just within the exit end of the furnace *J* about 5 inches (12.7 cm.) of coarsely granular cupric oxide held in place by two plugs of asbestos fiber.

The intake end of the combustion tube is fitted with a breech adapter which permits the introduction and removal of boats without disconnecting any rubber connections. The combustion may be observed through the cobalt glass window in the removable breech-block cap.

The temperature of the furnace, which should be maintained at about 950° C. within the tube, is controlled by the rheostat

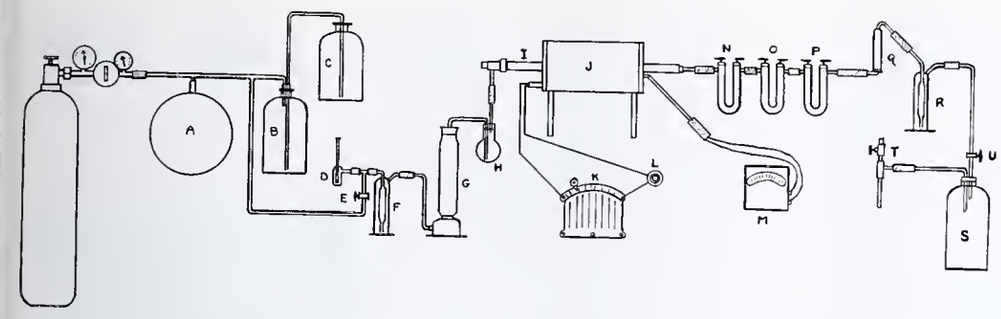

FIGURE 1. COMBUSTION TRAIN

K and measured by means of a pyrometer having the thermocouple placed in the position B indicated in Figure 2. A groove was filed in the inner circumference of the clay insulation as indicated to accommodate the thermocouple. The temperature difference measured by a thermocouple at this point B outside the refractory and that inside the silica tube A was determined and found to be constant after 90 minutes of heating. The temperature curves for the two points in the particular furnace used are given in Figure 3. A constant difference of 40° C. was reached and persisted after 90 minutes of heating.

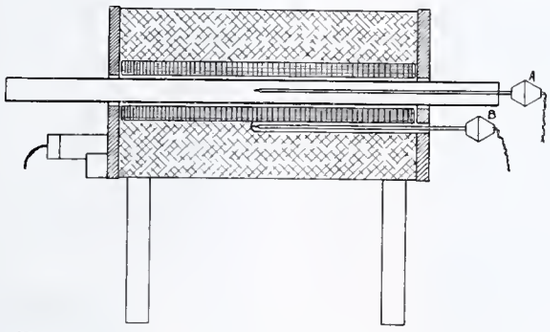

FIGURE 2. FURNACE, SHOWING POSITION OF COMBUSTION TUBE AND THERMOCOUPLE

The purification section of the train consists of three Schwartz drying tubes, charged with amalgamated 20-mesh zinc, N, sulfuric acid and glass beads, O, and phosphorus pentoxide or anhydrone, P. The use of the sulfuric acid tube lengthens the life of the charge in tube P and prevents clogging as would eventually occur if phosphorus pentoxide were used.

The absorption tube Q is made of a test tube by sealing a bent glass tube of small diameter into the bottom, and after charging with anhydrone and ascarite, as shown in Figure 4, the open end is closed with a stopper carrying a right-angle bent tube. The stopper is made air-tight with sealing wax in which the tube number is impressed with a metal die just before the wax is set. When not in use or being weighed, the open ends must be capped with rubber policemen. A tube made from a 1 × 6 inch (2.54 × 15.2 cm.) ordinary light-weight test tube will weigh when filled about 80 grams. If the quantities of carbon determined are small, a 0.625 × 6

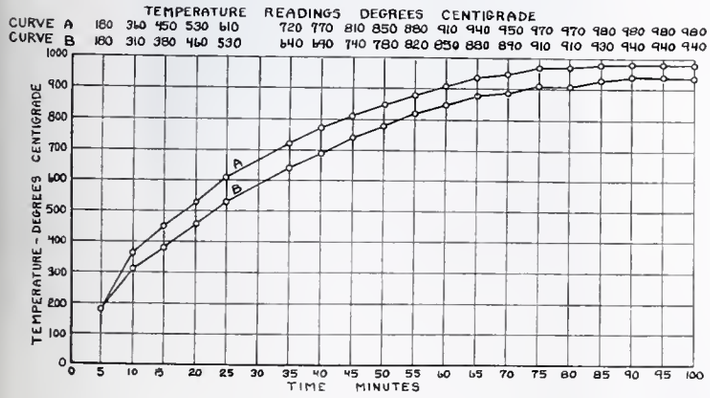

FIGURE 3. TEMPERATURE CURVES FOR FURNACE USED

inch (1.6 × 15.2 cm.) tube may be used, which, when filled, will weigh about 40 grams. Its low cost, light weight, and ease of wiping, and the fact that it can be hung on the hook of the balance stirrup for weighing are considerations which recommend this type of absorption tube. Such tubes can easily be made in the laboratory in quantity and their low cost hardly warrants cleaning for recharging for use again.

The scrubber R contains a 30 per cent solution of potassium hydroxide. Suction is applied through a large bottle, S, by an aspirator-type water pump T. The suction-equalizing bottle S aids in giving a steady suction, acting as a snubber or shock absorber.

The soil sample is mixed with 60-mesh carbon-free alundum or 60-mesh carbon-free alundum and manganese dioxide (*3*), using more alundum in proportion to the weight of the charge in cases of soils containing high percentages of organic matter. The combustion boats, preferably alundum, are introduced directly into the hot tube, previously heated to the operating temperature of about 950° C. The flow of oxygen is 100 to 200 cc. per minute, depending on the efficiency of the absorption tube, which in the case of the one here described depends on the diameter of the test tube from which it is made. The rate of gas flow can be regulated by placing a piece of capillary tubing of selected internal diameter and adjusted length in the rubber tube connecting the exit end of the absorption tube.

The usual details and precautions necessary in making the determination of carbon by use of this combustion train should be evident to any one familiar with dry combustion work. Results obtained with this combustion train have shown satisfactory agreement with theoretical values and satisfactory agreement of duplicate determinations. In the analysis of a series of 222 samples of soils which averaged 2.637 per cent of total carbon, the average difference between duplicates was 4.55 parts per 1000 parts of total carbon determined, a difference which compares favorably with results obtained by use of the procedures employed in general routine chemical analysis.

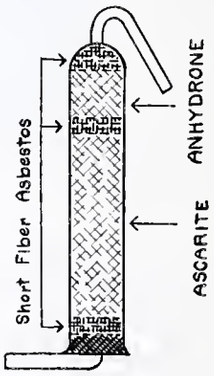

FIGURE 4. ABSORPTION TUBE

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RECEIVED December 30, 1932.

GERMAN VEGETABLE OIL-MILLING INDUSTRY SHOWS GAINS. Despite adverse conditions in world trade, the vegetable oil-milling industry of Hamburg is reported to have increased its output during the last few years, according to a report from the Department of Commerce.

Several large companies in and around Hamburg are said to be operating well toward capacity and oilseeds and fruits continue to be imported in large quantities. Business has been so well maintained that one of the companies has expanded its plant by the erection of several new buildings, and has augmented its working force by 450 new men.

An Automatic Pressure-Regulating Unit for Vacuum Distillation

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UNTIL recently organic chemists have paid slight attention to the accurate regulation of pressure during vacuum distillation. This condition has been largely due to the fact that no simple satisfactory device was available for general laboratory use. Under these circumstances there has been a tendency to avoid distillation under reduced pressure wherever possible or to adopt temporary hand-regulated makeshifts where its use became imperative.

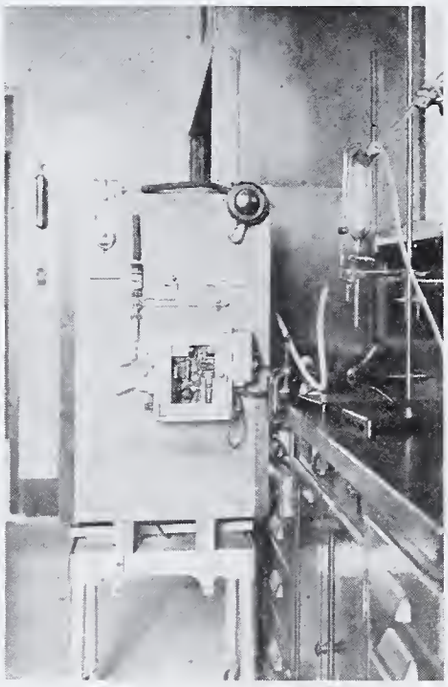

Figure 1. Pressure-Regulating Unit

Having occasion to prepare numerous compounds requiring vacuum distillation and finding no suitable control devices at hand, the authors have constructed a simple portable regulator capable of maintaining to ±0.15 mm. any pressure within the range of 2 to 30 mm., which has been used in these laboratories with great convenience and satisfaction.

Before designing the apparatus here described a survey of the literature since 1840 showed that more than thirty published descriptions could be classified as follows:

A. The pump operates continuously.
  1. A valve is interposed between the pump and the system.
     Mercury valve (*5, 16, 31*).
     Mechanical valve (*35*).
  2. A valve bleeds in air at atmospheric pressure.
     Mercury valve (*4, 8, 15, 19, 25, 33, 34, 37*).
     Mechanical valve (*1, 3, 6, 9, 11, 12, 17, 20, 21, 23, 24, 26, 27, 28, 29, 32, 36, 40*).
B. The pump operates intermittently (*7, 10, 13, 38, 39*).

In the present device (Figures 1 and 2) the pump operates intermittently. The pressure is reduced by means of a Cenco Hyvac pump operated by the usual 0.125-horsepower motor. Once the desired pressure has been attained, the pump is switched off by the action of a thermionic relay system (Figures 6 and 7) which is so connected with a manostat that it continues to turn the pump motor off or on as further fluctuations of the pressure may require. In order to make the apparatus of general utility this thermionic control has been so devised that it will without change operate upon either alternating or direct current, according to local facilities and the nature of the pump motor. That is, with an alternating current pump motor the relay system also operates on the same alternating current line; with a direct current motor the relay system operates on the same direct current line. Thus, for a given motor the entire apparatus is controlled by a single switch, and in actual use is simply brought up to and attached to the distillation system, plugged in to the power line, and allowed to maintain whatever pressure is desired according to the setting.

Associated with the pump and its thermionic control are the usual necessities of vacuum distillation, such as an absorption train (Figures 2 and 5) to protect the pump from vapors, a manometer for pressure measurement, and a manostat to effect operation of the thermionic relay. The entire ensemble is mounted on a light four-wheeled carriage, affording ready mobility from one place to another.

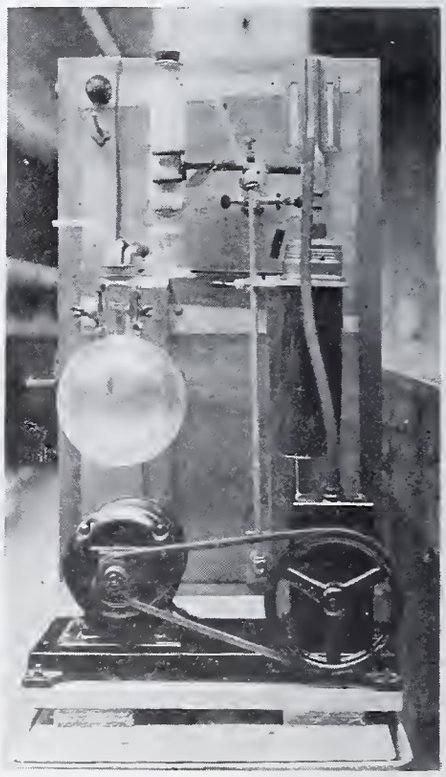

Figure 2. Pressure-Regulating Unit, Showing Absorption Train and Reservoir

The Manostat

This is essentially a U-manometer capable of being fastened in an inclined position. A fixed tungsten electrode contacts with the mercury, completing the relay circuit which controls the pump motor. Thus by tilting the manostat the

center of gravity is displaced, and the mercury will require a greater or lesser force, or vacuum, to bring it to that level at which it will make contact with the fixed electrode.

The manostat is of Pyrex glass, 14 cm. high with arms 2.5 cm. between centers and 7 mm. internal diameter. One tungsten contact is sealed through the concave side of the U-bend and the other through the top of the arm which connects with the system. The manostat is held near its upper end in a rotating clamp provided with a graduated radio dial for observation of the setting and a thumbscrew for clamping in a fixed position. Since the manostat is independent of variations of barometric pressure, a small graph relating the dial setting and pressure may be attached permanently to the panel for convenient reference.

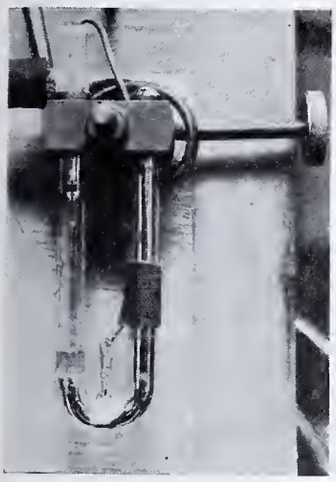

Figure 3. Manostat

Constriction of the manostat tubing is unnecessary, for in operation the apparatus panel is clamped against the laboratory desk and oscillation of mercury is negligible. Lubrication of the mercury in the open arm is infeasible, since the organic lubricant is slowly decomposed by the small thermionic current. The slight lag induced by the cohesion of the mercury and the tungsten is not serious, but may be avoided by the use of iron or nickel.

The Manometer

A small U-manometer 13 cm. high, with arms 4 cm. between centers, was constructed of Pyrex tubing of 7 mm.

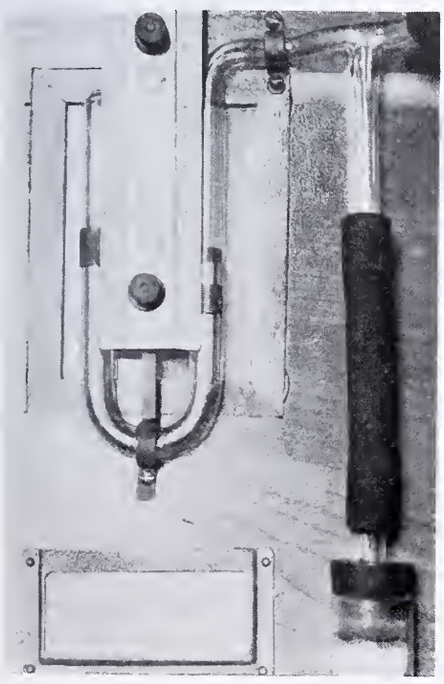

Figure 4. Manometer

internal diameter so as to be suitable for the measurement of pressures between 0 and 30 mm. of mercury. As shown in Figure 4, the open end terminates in a tee, one side of which connects with the manostat and the other through a short soda lime–activated carbon absorption tube to a three-way stopcock. Constriction of the manometer tubing is unnecessary, but the use of a lubricant, such as butyl benzyl phthalate or di-*n*-butyl phthalate saturated with diphenyl mercury or di-*p*-tolyl mercury (*18*), is recommended for increased sensitivity. A reading scale for the manometer is mounted on a square brass tube sliding on a square brass rod with a phosphor bronze friction spring. Parallax errors are avoided by observing the meniscus across brass rings blackened with ammonium sulfide and warmed over a flame

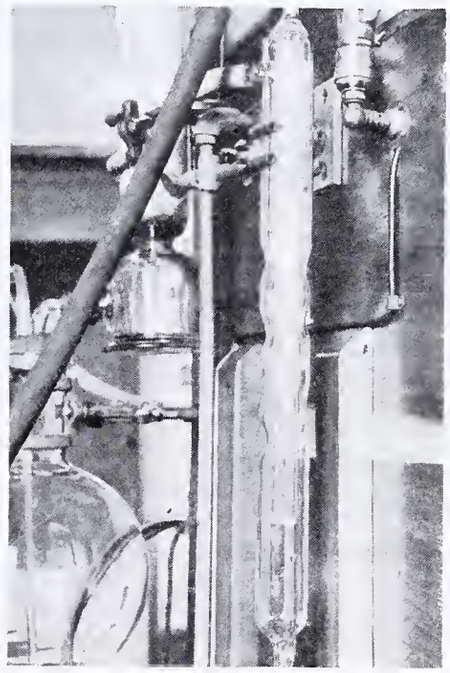

Figure 5. Absorption Train and Reservoir

(*30*). The right-hand ring is split and fastened to the sliding scale, the lower edge being set at the zero index. The left-hand ring is slipped over the closed arm and moves freely, with a friction spring holding it against the glass. To facilitate using the instrument at night, the manometer is illuminated from behind by a 25-watt lamp mounted on the back of the panel and shining through a double ground-glass window which protects from any heat. Both the manometer and manostat are protected from sudden access of air by means of a 10-mm. tube tightly packed with cotton and

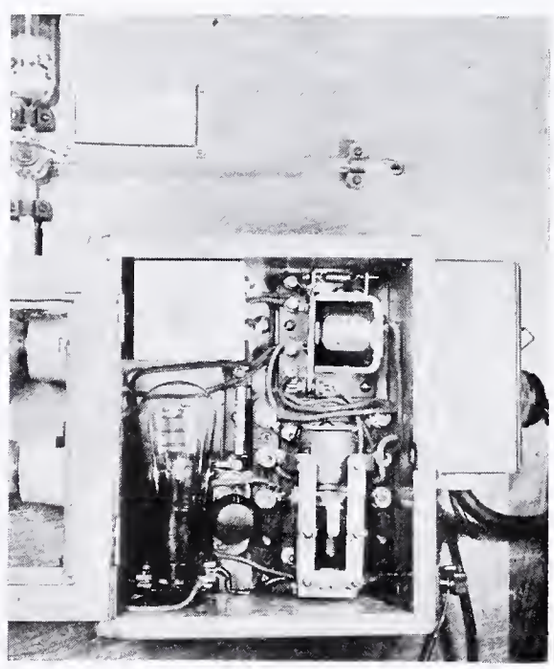

Figure 6. Relay Assembly

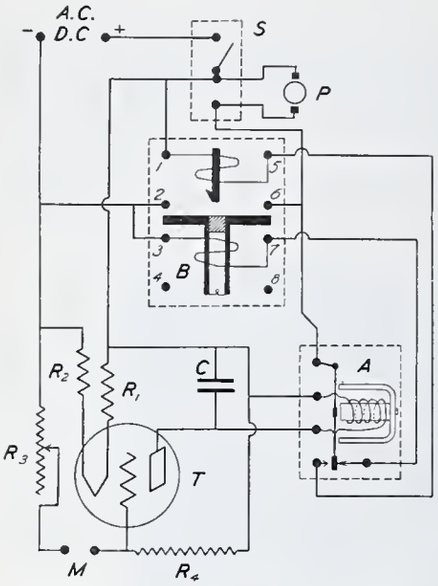

FIGURE 7. UNIVERSAL 110-VOLT THERMIONIC RELAY

A. Struthers Dunn, Inc., relay-type CXB-51, coil H. Coil resistance, 2700 ohms. Coil rating, 2 milliamperes. Contact rating, 2 amperes at 110 volts a. c.

B. Struthers Dunn, Inc., relay-type CS600. Contact rating, 30 amperes. Universal alternating or direct current. When assembling it is well to mount on sponge rubber to minimize noise.

C. 4-mfd. condenser. Rating, 300 volts direct current, 125 volts alternating current.

M. Manostat contacts.

P. Pump motor, 0.125 to 1 h. p. The rated operating current is usually much less than the starting current which must be broken at the contacts making necessary the auxiliary heavy-duty relay *B*.

R_1. 25-watt, 115-volt tungsten filament, G. E. Mazda lamp.

R_2. 40-watt, 115-volt tungsten filament, G. E. Mazda lamp.

R_3. Variable series resistor, 25,000–250,000 ohms range. This resistor serves as a fine adjustment to compensate for unavoidable variations in lamps R_1 and R_2 and in grid leak R_4. In practice this is adjusted to the highest resistance (and hence the smallest operating current) that will give dependable operation.

R_4. Grid leak, 8 megohms.

S. Single pole flush tumbler switch and plug receptacle for pump motor.

T. 71-A type tube, 5-volt filament. The filament should operate at a dull red heat with lamps R_1 and R_2 of the recommended rating.

attached through a 1-mm. capillary side-arm to the three-way stopcock mentioned above.

Absorption Train and Reservoir

For the protection of the pump it is necessary to provide for the removal of all condensable vapors from the gas stream. After considerable experimentation with various types and lengths of absorbents, the best combination was found to be a relatively short soda lime tower (Figure 2), for acid gases, together with a low temperature vapor trap, for water and organic liquids. The latter consists essentially of a suitable glass bulb trap (Figure 5) around which is raised a Thermos bottle (Figure 2) containing solid carbon dioxide and some low-freezing heat-transfer liquid. For the latter the authors prefer the use of a mixture of equal weights of chloroform and carbon tetrachloride (*22*), which avoids all fire hazard and upon whose surface the solid carbon dioxide floats. To facilitate cleaning out condensate from the glass bulb trap between runs without dismantling the train, a glass tube joined to the bottom of the trap is bent so as to extend out of the top of the bath as indicated. By blowing back through the usual connection to the distillation system the trap may readily be emptied.

Since the volume of the distillation system with which this regulator is ordinarily employed is relatively small as compared with the capacity of the pump it has been found desirable to include a reservoir in the system. For this purpose an ordinary 3-liter ring-neck Pyrex flask has served conveniently.

The Relay

The relay assembly shown in Figure 6 with wiring diagram in Figure 7 has been developed for the express purpose of controlling by means of a minute thermionic current the heavy starting load taken by the induction motor operating the pump. It is characterized by use of standard reproducible units, differing in this respect from that of Fergusen, van Lente, and Hitchens (*14*), by its relatively low cost, adaptability to common sources of power, and freedom from lag or fouling of the manostat contacts.

Application of a negative grid bias to the normally unbiased thermionic tube *T* (Figure 7) so diminishes the plate current that release of the sensitive relay *A* is effected (*2*). This action in turn controls the heavy-duty relay *B* operating the pump motor. The relay assembly is interchangeable on 110 to 115 volts alternating or direct current and all parts, including vacuum tube, condenser, relays, incandescent lamps, resistances, and switch, are standard commercial units. The relay may be enclosed in a wooden box or in a steel electrical cabinet 8 × 8 × 4 inches.

Pump and Carriage

The manostat, manometer, absorption train, reservoir, stopcock, and thermionic relay are all mounted upon a vertical wood panel as shown in Figures 1 and 2. This is supported by angle irons which join it to the frame of a small standard centrifuge carriage made by the International Centrifuge Corporation. The pump itself is mounted upon a wooden base, which rests in turn upon vibration insulating cushions of sponge rubber glued to the floating base of the carriage. The weight of the pump is sufficient to balance that of the panel and its equipment, and the entire stand is mechanically stable when being rolled from one place to another. When actually in use at a given spot, the vertical wood panel may be anchored to the desk by means of an angle iron and screw-clamp.

Acknowledgment

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A Laboratory Cooling Unit

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THE need for an adequate supply of cold water for chemical laboratories located in the tropics or in the southern part of the United States is often imperative. Pipes for city water supplies are in general laid close to the surface of the ground and become heated by the sun, and their contents attain temperatures comparable with their environment. A clever device for cooling a thermostat with cracked ice was reported recently (*3*), and many have had recourse to the time-honored method of running tap water through a metal coil immersed in a pail containing ice and water; but at best these are only makeshifts.

The use of refrigerating units for the laboratory is not new. Foote and Akerlof (*2*) have modified such a unit for thermostat control below room temperatures but the method as worked out in this laboratory does not seem to have been described before.

Construction of Cooling Unit

A small Frigidaire unit, model S, was modified as follows: Castors were mounted on the four short legs of the compressor frame and a handle was attached to one end of the frame. Four 17-inch steel rods were bolted to the corners of the frame in a vertical position, to support a wooden box of 0.5-inch stock, 22 inches long, 17 inches wide, and 20 inches deep, outside dimensions. This box was approximately the size of the frame of the unit, and was mounted above the compressor, clearing it by about 2 inches. A tank of heavy galvanized sheet iron, 15 inches long, 14 inches deep, and 11 inches wide, constructed to serve as a reservoir for the cooled water, was mounted in the wooden box and given a 2-inch clearance at the bottom by being supported on four wooden blocks. The expansion tank and cooling coil assembly of the Frigidaire unit was suspended in this galvanized iron tank, being supported by strap iron hangers from the rim with about 1-inch clearance between the cooling coils and the bottom of the water tank. The pipes from the compressor were led up through one corner of the wooden box and through a hole drilled in the wall of the water tank at a point about 2 inches below the rim. This allowed them to make their normal connection with the expansion tank at a slight slant so that any condensed gas could drain back to the compressor reservoir.

The air space between the walls of the wooden box and the metal water tank was insulated by packing with sawdust, and the last few inches near the top of the tank, above the water level, was tamped with newspaper. Two 0.385-inch copper pipes were introduced at one end of the assembly by drilling two holes, 9.5 inches apart, through the box and the iron tank, 2 inches below the rim of the tank. One pipe, to serve as the suction end for the pump, was bent at a right angle after entering the tank so that the end was about 0.5 inch from the bottom and would draw water from the coldest layer. The other pipe, for discharge, was continued on through the water tank to within an inch of the opposite wall and its tip bent down slightly, so the returning water would not splash and would help to maintain a good circulation around the cooling coils. The tank and all exposed metal parts were given a heavy coat of aluminum paint to prevent corrosion, or could be made of heavy sheet copper if the unit is to be placed in daily service. A hinged wooden cover, with 1.5-inch wooden batten that fitted the top of the water tank, completed this part of the assembly.

Outside the box, on a shelf below the two copper pipes, a small rotary water pump was mounted. A 0.1-horsepower synchronous motor from the laboratory was screwed to the other end of the shelf and belted to the pump. A snap switch mounted in the motor line completed this detail. Pump connections to the copper pipes and to any apparatus were made with rubber tubing.

A fuse block and double-pole single-throw switch mounted on the bottom of the wooden box safeguarded the compressor motor. A flexible lead attached ahead of this main line switch and brought up to the pump motor made the water circulation independent of the operation of the cooling unit. Ten feet of heavy-duty lamp cord, running from the fuse block and with plug attached, allowed the unit to be moved to any situation in the building and plugged into the nearest outlet.

Operating Data

Operating data on an apparatus of this type are only relative, since the efficiency is affected by room temperature, air movement, etc., while the total volume of water to be cooled, insulation of the tank, adequate stirring, etc., affect the rate of cooling.

The capacity of the water tank is about 24 liters, bringing the water level a little above the base of the expansion chamber and assuring good contact with all the cooling assembly. With the pump operating at about 750 r. p. m., 3.5 liters per minute of cooled water can be circulated through a Bailey-Walker extractor or through an ordinary glass condenser. With closed apparatus the discharge is under pressure from the pump and therefore the condenser or other apparatus can be located above or below the water level in the cooling tank. With connections open to the air, the discharge has to drain back to the tank by gravity and this fact should be kept in mind in designing the unit. A supplementary discharge pipe of 0.5-inch diameter may also be necessary where the flow is under a head of only 2 or 3 inches, in order to prevent backing up. The use of a direct current motor with variable-speed control for changing the rate of pumping might be of advantage. A convenience well worth installing is a 0.5-inch T connection soldered to the discharge pipe with the T inverted. A thermometer mounted in this vertical opening by means of a rubber stopper with the bulb projecting into the current of discharged water will give the temperature of the returned water and will indicate when the unit needs to be started or stopped.

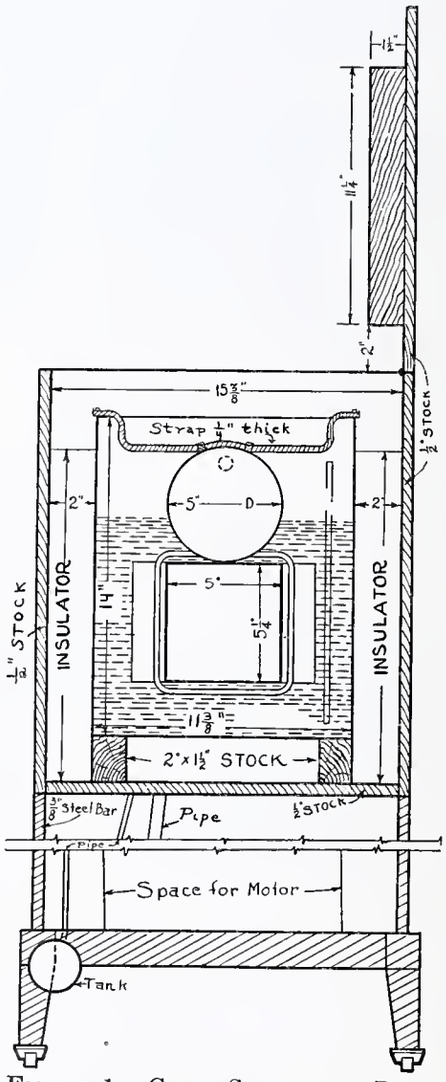

Figure 1. Cross Section of Box and Cooling Tank

In the normal operating range from 12° to 20° C. the unit

will give the hourly equivalent of the melting of 4.8 kilograms of ice. In actual practice, circulating water through a Bailey-Walker 6-unit extractor, using ether, and with no precautions to prevent radiation from the hot plate being absorbed by the water line, it was found possible to maintain the discharge water at a temperature from 16° to 20° C. by operating the compressor for 40 minutes and shutting it off for 30, while, if the temperature of the discharge was held between 18° and 24° C., 30 minutes' operation with one hour idle was possible. This intermittent operation could easily be made semi-automatic by introducing an interval timer and mercury contact relay in the power line of the compressor.

With better insulation and some other liquid than water, temperatures of 0° C. or below might easily be attained.

Though sawdust is not the best insulating material, the gain of heat from the outside is on the average 18 Calories per hour when the room temperature is from 25° to 28° C. and the tank temperature above 12° C. At lower temperatures the heat loss becomes greater. When cooled to 2° C., the tank water rose 3.6° in 3 hours, or an average gain of 28.8 Calories per hour.

With the tank water cooled to 6° or 8° C. a very short condenser serves efficiently, even with low boiling point petroleum ether. With longer condensers and this low-temperature cooling, high distillation rates can be maintained without loss, and it often becomes unnecessary to pack the receiver with ice. In humid climates condensation of water from the air may become a nuisance, but the wrapping of exposed parts with insulating material will obviate this to a large extent.

By circulating cooled water through a few coils of copper tubing immersed in a thermostat, the temperature of the latter may be maintained slightly below the regulating point, so that electric heating of the bath for regulation can be used as in colder climates.

This unit has also been found of service in photographic work. By the use of water-jacketed trays for developing, washing, and hypoing, the trays and their contents may be kept at any desired temperature. The cooling unit can be kept outside the dark room and the cooled water pumped through two pipes passing through the wall and connected with the jacketed trays. A switch located in the dark room and controlling the current in the compressor motor line gives adequate control of the temperature. Cooling machines (*1*) for commercial photographers are already on the market, but are too expensive for most institutions with only irregular demands on the dark room.

Acknowledgment

The author wishes to express his appreciation to Mr. Casaña for aid in assembling the unit and making various constructional details.

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An Inexpensive Muencke Blower

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A CURRENT of air of sufficient pressure to operate a blast lamp or a stirrer for the laboratory where the expense of a mechanical compressor is prohibitive can be obtained from a simple Muencke type of blower constructed from a varnish can and a few pieces of galvanized iron pipe and fittings together with an aspirator pump, as shown in the accompanying cross-sectional diagram.

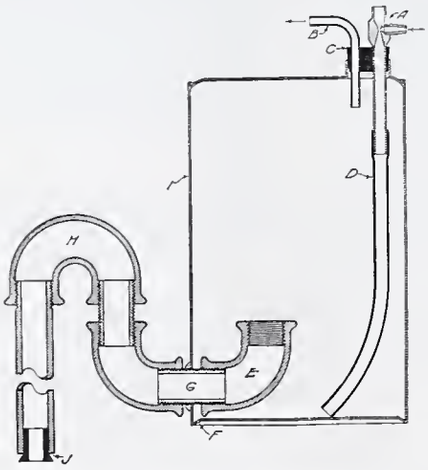

Figure 1. Diagram of Blower

A hole, just large enough to admit the nipple *G*, and a slit, upward from the hole, long enough so that the metal may be turned back to admit the elbow *E*, is cut in the side of the metal container *I*. The elbow and the nipple, connected, are then inserted, and the metal that has been turned back is pushed together. The slit and any space around the connecting nipple *G* are then closed tightly with solder. The soldering, with the aid of zinc chloride paste flux, is extremely easy because an ordinary can is already tinned. The remainder of the fitting is easily done and should be so arranged that the reverse elbow *H* is not more than one-half as high as the container.

A Boekel or straight aspirator pump *A* can be easily inserted, together with the air outlet tube *B* which may be made of glass or copper tubing, into a two-hole rubber stopper *C* in the mouth of the can.

The can should be set up at the edge of a sink, where drainage from the water outlet *J* and the nail hole *F* in the bottom of the can may be permitted. A piece of rubber tubing *D*, attached to the stem of the aspirator pump, decreases the splashing. Rubber stoppers with large holes may be inserted in the water outlet pipe *J* to adjust the water outlet flow. The inside diameter of the water outlet pipe should be at least twice that of the aspirator pump. An aspirator pump with 0.95-cm. (0.38-inch) iron pipe threads therefore requires a 1.9-cm. (0.75-inch) water outlet pipe at full main water pressure. A large bottle connected between the air outlet *B* and its point of use will aid in giving a steadier pressure.

The possibility of better design and method of construction of the blower are obvious, the above being merely a description of a blower which was improvised rather incidentally, but which has been in service for several years.

Received November 4, 1932.

A Stirrer Drive for Laboratory Use

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THE stirrer drive described in this paper is durable and can be easily constructed. The shaft holder *D* consists of a piece of steel 8.2 cm. (3.25 inches) long and 2.5 cm. (1 inch) in diameter, with a 1.3-cm. (0.5-inch) hole drilled lengthwise through it. *C* is an oil hole. Two 1.3-cm. (0.5-inch) iron rods, *H* and *G*, are welded to this shaft, 4.4 cm. (1.75 inches) apart. The upper rod *H* is 37.5 cm. (15 inches) long and the lower rod 22.5 cm. (9 inches). The shaft *F* is made of a seamless steel tubing 1.3 cm. (0.5 inch) outside diameter, 14 gage, and 27.5 cm. (11 inches) long. The shaft is slit lengthwise for 6.3 cm. (2.5 inches) and the four parts forced slightly apart, as indicated in Figure 1. A collar *E* made from brass tubing, 6.3 cm. (2.5 inches) long, is slipped over the lower part of the shaft. The pulley *A* is a three- or four-step pulley of 1.3-cm. (0.5-inch) bore and riding on a ball thrust bearing *B*.[1]

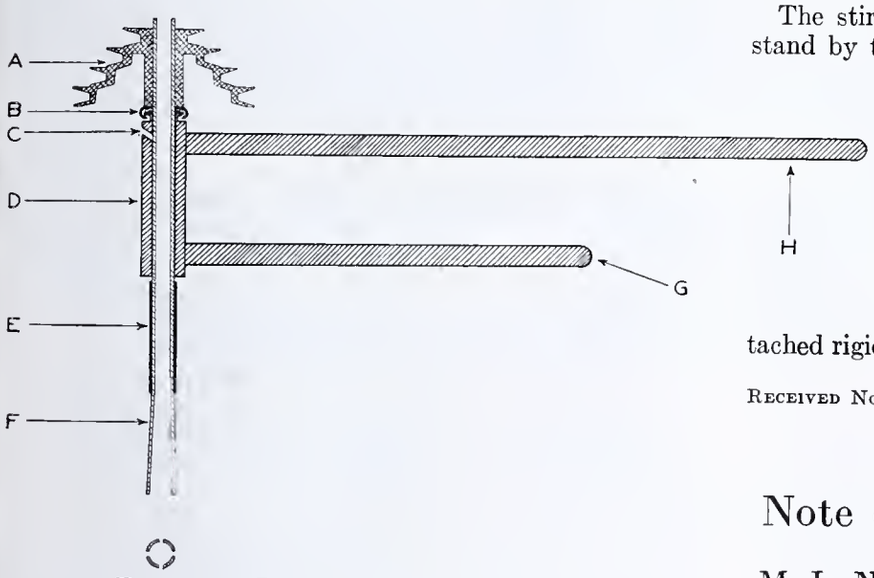

Figure 1. Diagram of Stirrer Drive

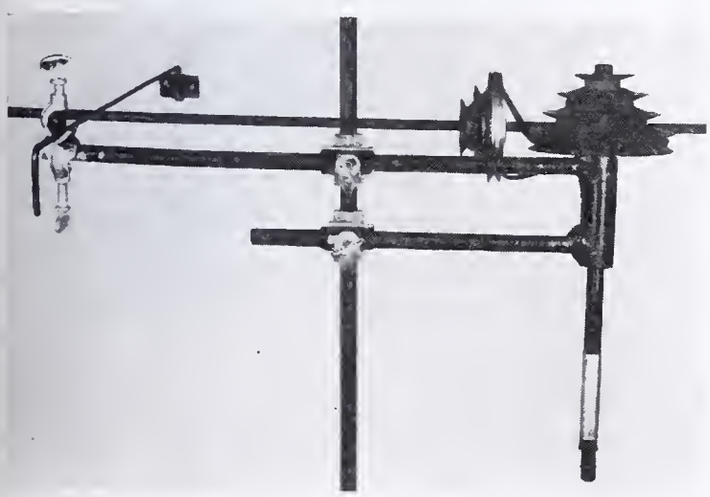

Figure 2. Stirrer Drive Fastened to Supporting Stand

Any glass stirrer up to 8 mm. outside diameter can be attached to this shaft. A small piece of rubber tubing is slipped over the glass rod, which is then inserted into the split shaft. When the brass collar *E* is moved downwards the shaft parts are pressed against the rubber and glass rod, holding it firmly in position. In other designs of stirrer holders the glass rod is held in position by a set screw, and often breaks at the point of application of the screw.

The stirrer drive is attached to the rod of a supporting stand by two large clamp fasteners, as shown in Figure 2. The upper rod *H* is attached to the wall by a curtain or welding rod to prevent the stirrer drive from slowly shifting around its vertical axis during operation.

The advantages of this stirrer holder are: Glass stirrers can be attached quickly by merely inserting the rod in the shaft and pulling down the collar; the glass rod is held firm in a rubber cushion; and the stirrer drive can be attached rigidly to a supporting stand.

[1] Manufactured by the Walker-Turner Co., Jersey City, N. J., and retailed through S. S. Kresge & Company and Sears, Roebuck & Company stores for fifty cents. The ball thrust bearing sells for twenty-five cents.

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Note on the Micro-Dumas Method

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IT OFTEN happens in this determination, especially with azotometers which have been filled with pure mercury, that the gas bubbles adhere to the interface between the mercury and the potash solution and can be loosened only by rather vigorous shaking. Pregl (*3*) says that "this occurrence, however, ceases after the first few determinations, when sufficient finely divided copper oxide dust has collected at the boundary between the two liquids." Flaschenträger (*1*) and Weygand (*5*) have advocated the artificial contamination of the mercury by the addition of finely divided copper oxide, but Meixner and Kröcker (*2*) state that this does not overcome the difficulty. Later Trautz (*4*) advocated the addition of some of the dark sludge formed by shaking mercury with ether.

Experience in this laboratory has shown that none of the above procedures are really effective in preventing the gas bubbles from adhering to the interface between the mercury and the potash solution. This difficulty, however, can be readily overcome, even in an azotometer filled with pure distilled mercury, by the addition of a small amount of mercurous oxide. The black oxide was prepared by treating some freshly precipitated calomel with the 50 per cent potash solution and washing thoroughly.

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A New Method for the Qualitative Detection of Casein in Woods

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THE process of treating woods with casein solutions is becoming very useful to such specialized industries as baseball bat, handle, and related manufacture. The usual method is to treat the wood with a solution of ammonium caseinate, ammonia, and lime with sufficient air pressure applied to increase penetration of the casein solution into the wood. Then a second treatment with either formaldehyde vapor or formaldehyde solution renders the casein insoluble in water (*2*).

The objects of this treatment are to prevent splitting of the wood on its surface and to render the surface waterproof, so that swelling will be prevented or greatly reduced. However, the treatment tends to reduce resiliency, it is important in the manufacture of these products to retain as much of the original resiliency of the wood as possible. Obviously then, it is valuable to be able to control the depth to which the casein solution penetrates, in order to obtain the optimum conditions for each wood. This can be done if this depth can be determined.

Experimental

The material used in these tests was obtained by cutting cross sections from the woods (ash, yellow poplar, and hickory) about 0.25 inch thick. This gave small disks, as the original samples were cylinders. The wood in each case had been thoroughly seasoned.

Neither the standard chemical tests nor several biological stains for casein worked on the casein-formaldehyde compound. However, a satisfactory method was obtained using Delafield's solution of hematoxylin.[1]

It was found that simply dipping sections in this stain, washing, and drying did not produce as clear-cut results as the following method:

Soak the section of wood to be tested in distilled water for at least 15 minutes. Remove and shake off excess water.

Dip the section into Delafield's solution of hematoxylin so that all the wood is covered for 2 minutes. Remove section and allow the excess stain to drain off into the solution. Rinse well with running water until all adhering stain is washed off.

Let it dry in the air.

A violet stain will be imparted to regions of the woods in which casein is present, but no such stain is found in either untreated woods or portions of treated woods into which the casein solution did not penetrate. The tint of the stain roughly indicates the amount of casein present.

[1] Mix a solution containing 4 grams of hematoxylin in 25 ml. of 95 per cent alcohol with 400 ml. of a saturated aqueous solution of ammonium alum. After standing in the air for 4 days, add 100 ml. of glycerol and 100 ml. of methanol. Cork well.

Quantitative Confirmation

Two disks of ash wood were stained as above to get indications of regions in which casein was present. The staining was identical in both sections. Three more disks were then cut from the same cylinder as the first two and divided into sections indicated by the stain. The first sections were taken from the outermost rim into the wood for 0.5 inch; the second sections from here into the wood for another 0.5 inch; the third sections were the remaining cores. Each section was analyzed for its nitrogen content according to the Kjeldahl method (*1*). Similar analyses were made on untreated wood to be used as blanks. The untreated wood sections showed an average nitrogen content of 0.03 per cent with very little variation. This was subtracted from determinations made on treated sections and the difference multiplied by 6.25 to convert nitrogen to casein. The results showed clearly that the stain was reliable:

Region	Staining	Casein Found
		%
Outer	Intense	2.7 –2.9
Middle	Faint	0.57–0.59
Inner	None	None

Discussion

Since it has been stated (*3*) that all calcium salts are stained by nuclear stains in microscopic work, it was necessary to eliminate this factor. Sections which had been treated with lime water only did not become stained by the method given in this paper; in a macro method of this kind calcium salts do not interfere.

It is believed that this method is applicable to the needs of other manufacturers of wood products. No elaborate technic or special apparatus is required, and the tests furnish a visible and permanent record which the plant manager can turn over to his executive for consideration.

Acknowledgment

The author gratefully acknowledges the help given by Julian Miller, Botany Department, University of Georgia.

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Toilet Preparation Production in Rumania. Rumanian production of toilet requisites, which is reported to be benefiting from the present tariff, amounted in 1931 to almost $1,000,000. Imports in the same year, shipped chiefly by France and Germany, totaled $250,000. Since exports of perfumes and cosmetics are negligible, Rumania's entire consumption of toilet preparations exceeded $1,200,000. Progress has been made likewise in the local manufacture of toilet soaps, but separate production figures on these soaps, as distinct from ordinary types, are not available. Total soap production in 1931 was $1,920,000 and imports, $113,000.

Many of the leading foreign manufacturers both of toilet preparations and soaps have made arrangements to manufacture their products locally, not alone because of duties but because raw materials are cheap and readily available. Since the population prefers products bearing foreign trade-marks, certain local producers have attempted to meet this requirement by purchasing manufacturing rights for foreign brands on a royalty basis. At present 90 per cent of the soap sold on the Rumanian market under foreign trade names is produced locally. The same applies to the majority of toilet preparations, including tooth pastes, mouth washes, powders, etc.

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Use of Stannous Chloride in Evaluation of Dye Mixtures

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IN THE evaluation of dye mixtures advantage is often taken of the difference in stability or ease of reduction in the presence of reducing agents. Titanous chloride is widely used in the estimation of dyes and under generally favorable conditions most dye mixtures are reduced with but slight evidence of selective action. Holmes (*3*), however, investigated a number of dye mixtures and demonstrated that under less favorable conditions the reduction of one dye often takes precedence over the other, or the one dye may not be reduced at all. Certain of the permitted food colors also exhibit this property. The azo dyes appeared to take precedence over the triphenylmethane group under the influence of titanous chloride, but as Holmes pointed out with several dye mixtures, the difficulty in the visual detection of the end point limited the practical utility. From this apparent difference in ease of reduction it appeared that many simple food dye mixtures might be evaluated by means of a set of reducing agents. In employing two such reagents there are two limiting conditions: (1) one agent shall be selective in its action, and (2) the reaction products of the first reduction shall not interfere with the action of the second agent. Evenson and Nagel (*2*) utilized ammonium sulfide in selectively reducing amaranth (C. I. 184) in presence of tartrazine (C. I. 640), the excess being destroyed by lowering the pH with sodium bitartrate, which also acted as a buffer for the estimation of the tartrazine with titanous chloride.

Stannous chloride and titanous chloride fulfil the requirements for a desirable set of reducing agents. The former is selective in its action and the stannic ions which are formed in a reduction do not react with the titanous ions in the subsequent titration of the second dye. Knecht and Hibbert (*5*) state that stannous chloride will reduce diamine sky blue (C. I. 518) in the presence of chrysophenin (C. I. 365), two azo dyes, and (*4*) that titanous chloride does not appear to react on stannic chloride nor stannous chloride with titanium tetrachloride, yet so far as the author is aware, these properties have never been employed in the evaluation of dye mixtures.

Among the permitted food dyes tested in this laboratory, it was interesting that the triphenylmethane group was sufficiently stable and four of the azo dyes sufficiently susceptible to the action of stannous chloride to permit evaluation of a simple mixture, one from each group.

MATERIALS

For convenience, the stannous chloride was made up approximately normal; 113 grams of tin chloride ($SnCl_2.2H_2O$) were dissolved in an equal number of cubic centimeters of hydrochloric acid and diluted to one liter. The dyes were of certified grade, made by various food color manufacturers. The titanous chloride solution was made and standardized according to the usual laboratory procedure (*4*). The sodium bitartrate used as a buffer was U. S. P. or C. P. quality.

SELECTIVE REDUCTION EXPERIMENTS

One per cent pure dye solutions of the food colors were made and standardized. Amaranth, ponceau SX, orange I (C. I. 85), and sunset yellow FCF were found to be rather readily reduced with stannous chloride. The reduction may be completed at room temperatures, and increasing the temperature only serves to speed up the reaction rate. Fast green FCF, guinea green B (C. I. 666), light green SF yellowish (C. I. 670), and brilliant blue FCF are but slightly attacked by stannous chloride, even on continued heating. Amaranth, particularly, reduced more rapidly in the presence of hydrochloric acid, but sodium bitartrate proved generally better. Buffers such as borax cannot be used in these dye mixtures, as the triphenylmethane dyes are not sufficiently stable toward stannous chloride at such an alkaline pH. From the standardized pure dye solutions, mixtures were made and the following procedure adopted:

Samples of a known mixture were pipetted into 1-liter wide-mouth Florence flasks. Fifteen grams of sodium bitartrate and water to bring the volume to 200 cc. were added. The solution was then heated and the number of cubic centimeters of 0.1 *N* titanous chloride for the reduction of both dyes determined under an atmosphere of carbon dioxide.

To one sample was added approximately 100 per cent excess of the amount of stannous chloride equivalent to the azo dye present (component A). The reaction was carried on according to the conditions given in Table I. The triphenylmethane dye (component B) was then determined by the usual titanous chloride titration. In order to approximate the excess for the azo dye, a trial reduction was first made, using twice the quantity of stannous chloride that would be necessary for the reduction of both dyes as indicated by the titanous chloride equivalent of the mixture. For example, 25.0 cc. of 0.1 *N* titanous chloride are required for a given mixture. Therefore, 5.0 cc. of normal

Table I. Typical Results by Selective Reduction

Series	Component Dyes	1% Dye Solution	N SnCl2 added	Time	Temperature	Component A Present	Component B Present	Component B Found	Difference
		Stannous Chloride Reduction							
		Cc.	Cc.	Min.	° C.	%	%	%	%
		30	4.5	3	80-100	91.2	8.8	11.0	+2.2
		30	3.8	3	80–100	75.2	24.8	25.8	+1.0
1	A, ponceau SX	50	4.6	3	80–100	54.2	45.8	48.4	+2.6
	B, guinea green B	50	2.1	3	80–100	25.5	74.5	74.4	−0.1
		100	1.8	3	80–100	10.3	89.7	89.8	+0.1
		100	0.6	3	80–100	3.5	96.5	96.5	0.0
2	A, sunset yellow FCF	40	5.1	18 hr.	20–25	75.8	24.2	25.6	+1.4
	B, brilliant blue FCF	110	1.7	18 hr.	20–25	9.5	90.5	90.5	0.0
3	A, orange I	60	2.0	24 hr.	20–25	19.3	80.7	79.3	−1.4
	B, light green SF yellowish								
4	A, amaranth	50	6.0	12	80–100	90.9	9.1	11.0	+1.9
	B, fast green FCF	100	1.2	12	80–100	9.1	90.9	91.7	+0.8

stannous chloride are used in the trial reduction. Subsequently, this trial reduction showed that component B used 15.0 cc. of 0.1 *N* titanous chloride and component A, by difference, needed 10.0 cc. Therefore, 2.0 cc. of 1.0 *N* stannous chloride represented approximately 100 per cent excess. The amounts of stannous chloride used, appearing in Table I, were ascertained by such a procedure.

In a mixture containing less than 40 to 45 per cent of component B, an additional step was necessary, because (1) estimations of small amounts of triphenylmethane dyes with titanous chloride invariably give high results; and (2) if a larger sample of mixture is taken, the high concentration of the stannic ions formed in the reduction of the azo dye restores the color of component B so rapidly after reduction by titanous chloride that quantitative estimation is uncertain. A known amount of component B was therefore added prior to the stannous chloride and subsequently subtracted from the final titration value obtained with titanous chloride.

Conclusion

The general utility of the set of reducing agents, stannous chloride and titanous chloride, in the evaluation of dye mixtures, has been investigated. Experimental evidence showed that mixtures of azo and triphenylmethane food dyes were satisfactorily analyzed. No doubt there are many dye mixtures whose components differ in ease of reduction in such a manner as to permit evaluation by a similar procedure.

The author wishes to thank O. L. Evenson, of this laboratory, for his helpful suggestions in performing and presenting this work.

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Volumetric Determination of Nitroglycerol and of Nitroglycerol and Dinitrotoluene in Admixture

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Practically theoretical results for nitroglycerol and for ethyleneglycol dinitrate may be obtained by dissolving the sample in acetic acid, adding an excess of ferrous chloride, hydrochloric acid, boiling, and then titrating the resulting ferric iron with standard titanous chloride solution, using ammonium thiocyanate as the indicator. When present in admixture, 2,4-dinitrotoluene does not interfere, and may be accurately determined in the residual solution by reduction with titanous chloride in the regular way. When present in small amount, diethyldiphenylurea or diphenylamine does not interfere.

Nitroglycerol may be conveniently determined by means of the du Pont nitrometer; the results obtained, however, are usually slightly low. Certain aromatic nitro compounds, such as dinitrotoluene, do not interfere in this nitrometer determination; compounds such as diethyldiphenylurea or diphenylamine, however, do interfere, because they undergo nitration in the decomposing bulb, and cause low results.

The nitrate groups in nitroglycerol may be reduced by suitable reagents, and the nitrogen determined as ammonia. In the method of Silberaad (*7*) the nitroglycerol in ether solution is partially reduced with sodium ethylate, then metallic zinc and iron are added, and the resulting ammonia is distilled into standard acid. In the method of Muraour (*6*) the nitroglycerol in acetone solution is treated with hydrogen peroxide, sodium hydroxide, and sodium perborate; after standing overnight Devarda's alloy is added, and the resulting ammonia distilled into standard acid. Muraour obtained results which closely checked the theoretical. Excellent results on the analysis of nitroglycerol were also obtained in this laboratory, but because of the time required for a determination, the method was not exactly suited to control analysis.

Dickson and Easterbrook (*2*) determined dinitrotoluene in admixture with nitroglycerol by reducing the latter with ferrous chloride in strong hydrochloric acid solution, then

extracting the unchanged dinitrotoluene with ether. Methylsulfuric acid may be used in place of ferrous chloride. Huff and Leitch (*4*) attempted to determine nitroglycerol in the presence of aromatic nitro compounds. The nitroglycerol and nitro compound were dissolved in acetic acid, hydrochloric acid was added, and then a known excess of ferrous sulfate. After boiling and evaporating to a small volume, the excess ferrous iron was titrated with standard potassium permanganate solution. Low results were obtained on nitroglycerol alone and in admixture with *p*-nitrotoluene. Several suggestions for methods of attack were given in their article, however. Their method was tried out in this laboratory, and low results for nitroglycerol were obtained consistently.

It was thought that the oxidized iron might be determined accurately without interference from glycerol, traces of nitric oxide, or possibly other substances. Knecht and Hibbert (*5*) first determined nitric acid by reduction to nitric oxide with ferrous iron, and titrating the resulting ferric iron with a standard solution of titanous chloride. The procedure finally developed was to dissolve the sample of nitroglycerol in acetic acid, add an excess of ferrous chloride, hydrochloric acid, and boil under a reflux condenser. After cooling, the ferric iron was titrated with standard titanous chloride solution, using ammonium thiocyanate as the indicator. An atmosphere of carbon dioxide was of course maintained in the titration flask during the entire procedure.

Preparation and Standardization of Solutions

A 0.2 *N* titanous chloride solution was prepared according to the directions of English (*3*). For each liter of solution, 150 cc. of 20 per cent titanous chloride and 100 cc. of concentrated hydrochloric acid were used.

For control work, a quick and accurate method of standardization is essential. Ferrous ammonium sulfate was used by Knecht and Hibbert (*5*). Thornton and Wood (*8*) recommend the use of Sibley iron ore. For the analysis of aromatic nitro compounds, Callan and Henderson (*1*) used titanous sulfate which had been standardized against recrystallized *p*-nitraniline. English (*3*) gave a comparison of this standard and ferrous ammonium sulfate. In the results reported in this article, ferrous ammonium sulfate was used as the ultimate standard.

The ferrous iron of the standard may be oxidized by several different methods. Potassium chlorate in hydrochloric acid solution was selected, as the excess oxidizing agent may be easily and completely destroyed by two evaporations to dryness. Knecht and Hibbert (*5*) suggest the use of a supplementary ferric alum solution for quickly checking the normality of the titanous chloride solution.

0.7 *N* Ferrous Chloride. For each liter of solution, 200 grams of ferrous chloride ($FeCl_2.4H_2O$) and 50 cc. of concentrated hydrochloric acid were used.

0.15 *N* Ferric Alum. For each liter of solution, 75 grams of ferric alum and 25 cc. of 95 per cent sulfuric acid were used.

Apparatus

The volumetric solutions were protected from the air, using an arrangement similar to that given by Knecht and Hibbert (*5*). Instead of hydrogen, carbon dioxide was used.

A special Florence-type titration flask with ground-in condenser was designed for this determination. The capacity of the flask is about 300 cc.; carbon dioxide is admitted by means of a short inlet tube on the shoulder. The ground-glass joint is No. 25 $\overline{\mathfrak{F}}$, rendering the condenser and flasks interchangeable. For a titration, the flask is fitted with a narrow one-hole rubber stopper, through which is inserted a short piece of 8-mm. glass tubing.

Determination of Nitroglycerol

Weigh 1.8 to 2.0 grams of nitroglycerol, dissolve in glacial acetic acid, and make up to volume in a 250-cc. volumetric flask. Displace the air in a special titration flask by passing in a current of carbon dioxide for about 5 minutes. By means of an accurate pipet, transfer a 25-cc. aliquot portion of the acetic acid solution to the flask. Add 15 cc. of ferrous chloride solution and 25 cc. of hydrochloric acid (1 to 1) in the order named, connect the flask to the reflux condenser, and boil gently for 5 minutes. A few glass beads may be added to prevent bumping.

Increase the current of carbon dioxide, then cautiously immerse the flask in a large beaker of cold water, keeping the index finger over the top of the condenser until the hot vapors are condensed. After cooling to room temperature, disconnect the condenser, insert the one-hole rubber stopper, and titrate with the titanous chloride solution until near the end point. Add 5 cc. of 20 per cent ammonium thiocyanate solution and continue the titration until the red color of ferric thiocyanate just disappears.

Determine the small amount of ferric iron in the ferrous chloride solution and traces of interfering impurities in the reagents by running a blank under the same conditions as for a sample, and make the necessary correction.

The results obtained on a sample of filtered nitroglycerol and on a sample of ethyleneglycol dinitrate are given in Table I.

Table I. Purity of Nitroglycerol and of Ethyleneglycol Dinitrate

Method	Nitroglycerol	Ethyleneglycol Dinitrate
	%	%
Nitrometer	99.21	99.21
$FeCl_2$-$TiCl_3$	99.84	99.92
	99.94	99.87
	99.88	99.86

Determination of 2,4-Dinitrotoluene and Nitroglycerol in Admixture

The determination of dinitrotoluene alone is usually carried out by dissolving the weighed sample in alcohol, acidifying with hydrochloric acid or sulfuric acid, adding a 100 per cent excess of titanous chloride or sulfate, and boiling. After cooling, the excess reducing agent is titrated with a ferric alum solution, using ammonium thiocyanate as the indicator.

In the determination of dinitrotoluene in admixture with nitroglycerol, the latter would interfere if the foregoing procedure were used. It was found, however, that the dinitrotoluene did not interfere in the method developed for the determination of nitroglycerol. Under the conditions of the determination, the 5 minutes' boiling with ferrous chloride did not reduce the dinitrotoluene. At room temperature, the ferric iron formed by the reduction of the nitroglycerol could be titrated to a sharp end point by the titanous chloride solution, in the presence of the dinitrotoluene. It was also found that the dinitrotoluene could then be determined in the residual solution in the usual way.

Procedure. Dissolve the weighed sample of nitroglycerol and dinitrotoluene in acetic acid and make up to volume in a 250-cc. volumetric flask. Transfer a 25-cc. aliquot portion to a titration flask, and proceed exactly as in the determination of nitroglycerol alone, taking care to titrate just to the end point.

Add a 100 per cent excess of titanous chloride solution, again connect the flask to the reflux condenser, and boil for 5 minutes. Cool the flask and contents to room temperature and titrate the excess reducing agent with the ferric alum solution.

Run a blank determination, adding equal quantities of the reagents, and having ascertained the slight loss of titanous chloride on boiling, apply the proper correction in calculating the results.

It will be observed that a few conditions are different from those that prevail in the usual determination of dinitrotoluene. The nitro compound is boiled with titanous chloride in the presence of ferrous chloride and ammonium

thiocyanate. The indicator was found to have no effect. Ferrous chloride, however, will reduce the nitro compound to a slight extent, unless some ferric iron is present. The amount of ferric iron necessary to prevent reduction of the dinitrotoluene during the nitroglycerol determination does not appear to be critical, as is shown by the results given in Table II, on two typical laboratory samples.

Table II. Effect of Excess of Ferrous Chloride on Determination of Dinitrotoluene and Nitroglycerol in Admixture

$FeCl_2$ Added	Nitroglycerol	Dinitrotoluene
Cc.	%	%
15	5.03	6.63
	5.07	6.59
5	5.06	6.58
15	20.23	2.00
20	20.24	1.98

The results obtained on a sample of dinitrotoluene and on a known mixture of nitroglycerol and dinitrotoluene are given in Table III.

It was found that small amounts of diethyldiphenylurea or diphenylamine did not interfere in the determination of nitroglycerol and dinitrotoluene by the use of the foregoing method.

Table III. Determination of Nitroglycerol and Dinitrotoluene in Admixture

Nitroglycerol Found	Dinitrotoluene Found
%	%
.....	99.28
.....	99.22
99.87	99.36
99.90	99.26

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Indicators for Determining Chromium and Vanadium in Alloy Steels

Oxidized Diphenylamine Sulfonic Acid and Oxidized Diphenylamine

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This paper describes an investigation of the properties of diphenylamine sulfonic acid as an indicator for chromium and vanadium in tungsten steels. With a preliminary oxidation of diphenylamine sulfonic acid, the blank correction to be applied when using this indicator is reduced to a very small value. It is sufficiently constant with definite procedures to give very accurate results for chromium or vanadium.

A preliminary oxidation of diphenylamine completely eliminates a blank correction for this indicator when used in vanadium or chromium determinations.

Diphenylamine sulfonic acid is an oxidation-reduction indicator which may be used in the presence of tungstic acid, but its properties under such conditions have not been thoroughly tested (*4*). It has been used in the analysis of chrome-vanadium-tungsten steels for vanadium (*8*). Though accurate results were obtained, the indicator blank which had to be applied, because of reduction of some vanadic acid by the indicator, was undesirably large. It was noted in this paper (*7*) that an indicator with no blank correction could be prepared by a preliminary oxidation, but this is only approximately true.

Since diphenylamine and diphenylbenzidine are of no value in the presence of tungstic acid (*6*), it seemed important to study the properties of an indicator not affected by this substance. Methods for chromium or vanadium which do not involve the removal of tungstic acid and the determination of the small amount of vanadium which inevitably accompanies the precipitate are obviously much more rapid and simple.

Experimental

Preparation of Indicator. A 0.01 *M* solution of diphenylamine sodium sulfonate is prepared by dissolving 3.2 grams of the barium salt (obtainable from the Eastman Kodak Co., Rochester, N. Y.) in a liter of water, adding to this solution a slight excess of sodium sulfate, and decanting or filtering the solution.

Preparation of Oxidized Indicator. The volume of the 0.01 *M* indicator solution specified in a given experiment is placed in a small beaker, 5 cc. of water, 3 or 4 drops of concentrated sulfuric acid, and 3 or 4 drops of 0.1 *N* potassium dichromate are added, and then very dilute ferrous sulfate (0.01 to 0.02 *N*) is added until the purple color, which appears on the addition of the first few drops of ferrous sulfate, just turns to a bluish green. As this purple color begins to disappear, the ferrous sulfate should be added in parts of a drop, in order to have no excess present in the oxidized indicator solution. This bluish green solution is added to the solution to be titrated. In the experiments described in this paper the oxidized indicator was prepared in separate samples for each titration.

A stock solution of the oxidized indicator is often more convenient and may be prepared as follows:

One hundred cubic centimeters of 0.01 *M* diphenylamine sodium sulfonate and 25 cc. of concentrated sulfuric acid are diluted to 900 cc. in a liter volumetric flask. To this solution 25 cc. of

0.1 N potassium dichromate are added slowly with frequent shaking, followed by 0.1 N ferrous sulfate with repeated shaking, until one drop causes a visible change in color from bluish green to a clear deep green in the liquid when viewed through the neck of the flask. This will require approximately 6.5 cc. of ferrous sulfate.

Since the indicator will slowly settle out of this solution, it must be shaken before using. To avoid this as well as the necessity for adding an exact amount of ferrous sulfate, the precipitate may be washed free from acid and salts and then stirred up with water in which it remains as a colloidal solution. This is done as follows:

One hundred cubic centimeters of 0.01 M diphenylamine sodium sulfonate and 5 cc. of concentrated sulfuric acid are diluted to about 300 cc. To this liquid 25 cc. of 0.1 N potassium dichromate are added slowly, followed by 8 cc. of 0.1 N ferrous sulfate. This green solution is allowed to stand 3 or 4 days, until a portion of the supernatant liquid gives no color when added to 100 cc. of water containing 2 cc. of 0.1 N potassium dichromate and 5 cc. of concentrated sulfuric acid. Then the supernatant liquid should be siphoned off slowly, care being taken not to disturb the green precipitate which is the indicator. Three hundred cubic centimeters of water and 15 cc. of concentrated sulfuric acid are added to the precipitate, the latter is allowed to settle again, and the supernatant liquid is siphoned off. More thorough and rapid washing can be obtained by centrifuging. The green precipitate is then shaken up with 100 cc. of water. In the absence of electrolyte the precipitate will not settle out appreciably; even when not centrifuged, it settles very slowly and requires only occasional shaking. One-half cubic centimeter of this mixture gives the same color intensity in a titration as 0.3 cc. of 0.01 M diphenylamine sulfonic acid, and therefore may be substituted for it.

Relative Blanks for Oxidized and Unoxidized Indicator. Twenty cubic centimeter portions of 0.05 N potassium dichromate solution were treated with 5 cc. of sulfuric acid (specific gravity 1.5) and 5 cc. of phosphoric acid (specific gravity, 1.37), and diluted with water to 200 cc. Three of these samples were titrated with 0.025 N ferrous sulfate after adding 0.3, 0.6, and 0.9 cc. of 0.01 M unoxidized indicator, and three more were titrated after adding these same volumes of 0.01 M indicator which had been oxidized. For the first three samples the blanks in 0.025 N ferrous sulfate were 0.30, 0.56, and 0.79 cc., respectively; for those containing the same volumes of indicator in oxidized form, the blanks were 0.15, 0.38, and 0.57 cc.

The theory has been advanced (*4*) that the first step in the oxidation of diphenylamine sulfonic acid is to diphenylbenzidine sulfonic acid, and the next to diphenylbenzidine sulfonic acid violet, which in turn may form a meriquinoid compound, diphenylbenzidine sulfonic acid green, with unoxidized diphenylbenzidine sulfonic acid, or may form higher oxidation products if any excess of oxidizing agent is present. If this explanation is correct, the use of the oxidized indicator in titrations of chromic or vanadic acid with ferrous sulfate should eliminate any blank correction due to the first step in the oxidation of the indicator, an irreversible reaction, and, since the next step in the oxidation represents a reversible reaction, should cause any blank correction to be due mainly to the irreversible reactions represented by the oxidation of diphenylbenzidine sulfonic acid violet, which means destruction of the indicator, some loss of which is inevitable.

To determine the indicator blanks with variations in concentration of oxidizing agent, volume of solution, acidity, and volume of oxidized indicator, measured portions of a standard solution of potassium dichromate prepared from material of accurately determined oxidizing power were taken, treated with a definite volume of sulfuric, and of hydrofluoric or phosphoric acid, and diluted to the volume specified in Table I. The stated volume of 0.01 M indicator, oxidized, was added and the chromic acid titrated with 0.025 N ferrous sulfate standardized electrometrically against standard ceric sulfate (*8*), the strength of which had been determined against Bureau of Standards sodium oxalate (*8*). From the normality of the ferrous sulfate the volume of reducing agent equivalent to the dichromate present was calculated, and the difference between this value and the actual value obtained in the titration, using the indicator, was recorded as the apparent indicator blank. The results are given in Table I. Some of the values in the last column in this table involve more than the true indicator blank, as the volume of ferrous sulfate required to titrate a given amount of dichromate varies with the concentration of the latter (*1*, *5*) and is reduced slightly by hydrofluoric acid if present in sufficient concentration (*1*).

Table I. Titration of Dichromate with Diphenylamine Sulfonic Acid as Indicator

Expt.	$K_2Cr_2O_7$ 0.05N	H_2SO_4 Sp. Gr. 1.5	HF 48%	H_3PO_4 Sp. Gr. 1.37	Indicator 0.01 M, Oxidized	Initial Volume	Apparent Indicator Blank for 0.025 N $FeSO_4$
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
1	25	5	5	..	0.3	200	0.28
2	25	5	5	..	0.3	100	0.31
3	25	5	5	..	0.3	300	0.26
4	15	5	5	..	0.3	200	0.26
5	5	5	5	..	0.3	200	0.22
6	25	5	5	..	0.5	200	0.50
7	25	5	.	5	0.3	200	0.13
8	25	5	.	10	0.3	200	0.15
9	25	5	.	20	0.3	200	0.17
10	25	10	.	5	0.3	200	0.12
11	25	20	.	5	0.3	200	0.13
12	25	5	.	5	0.6	200	0.40
13	25	5	.	5	0.9	200	0.59

With the solutions containing hydrofluoric acid, there was a slight return of purple after the end point was apparently reached, and an additional 0.04 to 0.08 cc. of 0.025 N ferrous sulfate was required to obtain a permanent end point. This latter volume of ferrous sulfate is the one recorded above. From experiments 1 to 5 it is seen that variations in volume and in concentration of dichromate cause only a very slight change in the indicator blank and from 7 to 11 that the blank in phosphoric acid solutions is consistently lower than in hydrofluoric acid solutions. Experiments 7 to 11 also show that the blank is independent of acid concentration, while 6, 12, and 13 indicate that the blank is greatly influenced by the volume of indicator used, because the destruction of the latter is greater the greater the concentration. The end-point color change was less sensitive in 10 and 11, in which considerable acid was present.

Indicator Blank in Titrations of Vanadic Acid in Tungsten Steels

Since one of the most important uses of diphenylamine sulfonic acid is for titrations of vanadic acid in chrome-vanadium-tungsten steels, the effect on the indicator blank of changes in concentration of vanadium was studied.

To 0.8-gram samples of ingot iron, potassium dichromate equivalent to 0.035 gram of chromium, measured portions of an ammonium vanadate solution, and 5 cc. of sulfuric acid (specific gravity, 1.83) were added. After the iron was dissolved, nitric acid (specific gravity, 1.42) was added, drop by drop, to the hot solution, about 5 cc. being used in all, and the solution was boiled 2 to 3 minutes to remove oxides of nitrogen. After diluting to 160–175 cc. and cooling to room temperature, 5 cc. of hydrofluoric acid (48 per cent) and sodium tungstate solution equivalent to 0.2 gram of tungsten were added. The permanganate-azide method (*7*) was used to convert the vanadyl salt into vanadic acid. Then 3 cc. more of hydrofluoric acid (48 per cent) and 0.5 cc. of 0.01 M indicator, oxidized, were added, and the vanadic acid titrated with 0.025 N ferrous sulfate standardized electrometrically against standard ceric sulfate.

The results obtained are given in Table II, each value in the second and third columns representing an average of three duplicate determinations.

Table II. Change in Value of Indicator Blank with Change in Vanadium Present

Vanadium Present	Indicator Blank Expressed in Terms of: $FeSO_4$, 0.025 N	Vanadium in 1-gram sample of steel
Gram	*Cc.*	%
0.0048	0.02	0.002
0.0096	0.12	0.015
0.0144	0.22	0.027
0.0240	0.18	0.023
0.0336	0.18	0.023

For amounts of vanadium ranging from 0.96 to 3.36 per cent the error is small and sufficiently constant so that it may be eliminated by a proper correction.

Experiments were also carried out with the quantity of vanadium kept constant to note the effect on the indicator blank of changes in volume of indicator used. For this purpose 1-gram samples of Bureau of Standards steel 50 (*a*), containing 0.976 per cent of vanadium, were taken and the permanganate-azide method (*7*) was used. Before titrating the vanadic acid with ferrous sulfate, standardized against ceric sulfate, 3 cc. of hydrofluoric acid (48 per cent) and the indicated quantity of 0.01 M indicator, which had been oxidized, were added to the solution, approximately 200 cc. in volume. The results are given in Table III.

Table III. Change in Value of Indicator Blank for Vanadium Determinations with Change in Volume of Indicator

Indicator 0.01 M, Oxidized	Indicator Blank Expressed in Terms of: $FeSO_4$, 0.025 N	$FeSO_4$, 0.025 N, per 0.1 cc. indicator	Vanadium Found after Applying Blank of 0.05 cc. 0.025 N $FeSO_4$ per 0.1 cc. Indicator
Cc.	*Cc.*	*Cc.*	%
0.3	0.01, 0.12, 0.07	0.023	0.994, 0.980, 0.986
0.6	0.29, 0.31, 0.25	0.047	0.997, 0.975, 0.982
0.9	0.49, 0.54, 0.47	0.055	0.971, 0.964, 0.973
1.2	0.54, 0.54, 0.59	0.047	0.984, 0.984, 0.977
1.5	0.84, 0.82, 0.82	0.056	0.966, 0.967, 0.967

With 0.6 to 1.5 cc. of indicator, the blank varies in direct proportion to the volume of indicator used, while with 0.3 cc. of indicator the blank is slightly smaller. The larger blank obtained with chromic acid is explained by the fact that vanadic acid is a weaker oxidizing agent and destroys less indicator. According to the data in Table III one would expect the second value in Table II, column 2, to be approximately 0.24 cc. This discrepancy between synthetic samples and steels, though often observed, has not yet been satisfactorily explained.

If the 0.025 N ferrous sulfate to be used for vanadium determinations in tungsten steels is standardized according to the procedure in experiment 7, 8, or 9 in Table I, using that quantity of dichromate which will require 35 to 40 cc. of the reducing agent, and if the vanadium is determined by the permanganate-azide method, it might be expected that no blank correction would be required with 0.3 cc. of 0.01 M indicator, oxidized, and that a correction of +0.10 cc. of 0.025 N ferrous sulfate would be necessary with 0.5 cc. of the same indicator when oxidized. This was tested by determinations of vanadium in Bureau of Standards steel 50 (*a*), containing 0.976 per cent of vanadium. With three samples, for each of which 0.3 cc. of 0.01 M indicator, oxidized, was used, a blank correction of +0.05 cc. of 0.025 N ferrous sulfate was applied, resulting in 0.980, 0.974, and 0.978 per cent of vanadium, while with three other samples for which 0.5 cc. of the same indicator was used, a blank correction of +0.10 cc. gave 0.978, 0.981, and 0.961 per cent of vanadium. From Tables I, II, and III it might be assumed that when 0.3 cc. of the 0.01 M indicator in oxidized form is used in a vanadic acid titration in a 1-gram sample of steel, the blank correction should be −0.10 cc. if the vanadium is less than 0.85 per cent, +0.05 cc. for 0.85 to 1.2 per cent of vanadium, and +0.10 cc. for 1.2–3.5 per cent of vanadium, provided that the ferrous sulfate has been standardized against dichromate according to the procedure in experiment 7, Table I. Three analyses of Bureau of Standards steel 50, containing 0.756 per cent of vanadium, gave, after a blank correction of −0.10 cc. of 0.025 N ferrous sulfate, 0.756, 0.760, and 0.756 per cent of vanadium.

Indicator Blank in Titrations of Chromic Plus Vanadic Acids in Tungsten Steels

To 0.8-gram samples of ingot iron, potassium dichromate solution equivalent to the quantities of chromium specified in Table IV and 5 cc. of sulfuric acid (specific gravity, 1.83), were added. After the iron was dissolved, hydrofluoric acid followed by nitric acid was added and the solution boiled to remove oxides of nitrogen. The chromium was oxidized by the usual persulfate method with silver ion as catalyst. (The details of this new procedure for chromium in tungsten steels are given in the following paper.) Before titration of the chromic acid with 0.05 N ferrous sulfate, a little hydrofluoric acid, sodium tungstate solution equivalent to 0.2 gram of tungsten, and 0.3 cc. of 0.01 M indicator, which had been oxidized, were added. The volume of solution at this point was 300 cc. The ferrous sulfate solution was restandardized according to experiment 7, Table I, for each set of experiments listed in Table IV. An amount of dichromate approximately equivalent to that present in the samples was used for this purpose. It was found in this way that the normality of the ferrous sulfate was the same over the entire chromium range in Table IV. Therefore, in all later standardizations of ferrous sulfate against dichromate, using oxidized diphenylamine sulfonic acid as indicator, that amount of standard dichromate requiring 35 to 50 cc. of the ferrous sulfate was used, and the procedure of experiment 7, Table I, was followed.

Table IV. Titration of Dichromate after Persulfate Oxidation

(Ferric iron and tungstic acid present, oxidized diphenylamine sulfonic acid as indicator)

Chromium Present	Chromium Found after Correction of −0.15 cc. of 0.05 N $FeSO_4$
Gram	*Gram*
0.0131	0.0129, 0.0130, 0.0130
0.0218	0.0218, 0.0219, 0.0218
0.0305	0.0304, 0.0304, 0.0304
0.0392	0.0393, 0.0393, 0.0393
0.0479	0.0478, 0.0479, 0.0478

When duplicate samples of a standard dichromate solution were titrated with 0.05 N ferrous sulfate, using the procedure of experiment 7, Table I, the ferrous sulfate was 0.05090 N. This same ferrous sulfate when standardized electrometrically against standard ceric sulfate was 0.05073 N. As this last method is known to be correct, a blank of −0.15 cc. of 0.05 N ferrous sulfate must be applied to volumes of this reagent used in chromic acid titrations if the reducing agent has been standardized against dichromate by the procedure above, using as indicator 0.3 cc. of 0.01 M diphenylamine sulfonic acid which has been oxidized. The data in Table IV to which this blank correction of −0.15 cc. has been applied show that this indicator method for chromium is quantitative over the range of chromium content usually encountered in tungsten steels. For some unexplained reason the color change at the end point in the experiments in Table IV was never as sharp as in samples of steels.

To study the effect on the indicator blank of changes in the volume of oxidized indicator used, 1-gram samples of Bureau of Standards steel 50 (*a*), containing 3.52 per cent of chromium, were taken, and the chromium and vanadium oxidized by the usual persulfate method with silver ion as catalyst, hydrofluoric acid being present throughout the analysis to keep the tungstic acid in solution. Before the titration a

little more hydrofluoric acid and the indicated volume of 0.01 *M* indicator, oxidized, were added to the solution, approximately 300 cc. in volume. The results are given in Table V, each blank recorded being an average of three determinations. The values in the second column are the variations from the calculated volume of 0.05 *N* ferrous sulfate for the chromic acid, obtained from standardizing it against dichromate, using the procedure in experiment 7, Table I. The values in the third column are the variations from the theoretical volume of 0.05 *N* ferrous sulfate required for the chromic acid when the ferrous sulfate is standardized electrometrically against standard ceric sulfate.

Table V. Change in Value of Indicator Blank for Chromium Determinations in Tungsten Steels with Change in Volume of Indicator

Indicator 0.01 *M*, Oxidized	Blank in 0.05 *N* $FeSO_4$ Standardized against: $KrCr_2O_7$, using indicator	$Ce(SO_4)_2$ electrometrically	Chromium Found after Application of Indicator Blank in Second Column
Cc.	*Cc.*	*Cc.*	%
0.3	−0.36	−0.23	3.53, 3.53, 3.51
0.6	−0.13	−0.07	3.52, 3.51, 3.53
0.9	+0.07	+0.20	3.53, 3.52, 3.51
1.2	+0.10	+0.23	3.52, 3.51, 3.53

The results in the last column show the close agreement between experiments in which the same volume of indicator is used. Obviously one would always expect larger positive values in the third column than in the second, as the correct normality of the ferrous sulfate by standardization electrometrically against ceric sulfate is smaller than the normality against dichromate using the indicator. It is especially difficult, however, to give a reason for any negative indicator blank in the third column. Whatever is responsible for the uniformly low blanks in this column must exert a like influence in making the second column blanks of smaller positive value than one would anticipate.

Though this unexplained discrepancy in Table V, amounting to approximately 0.1 mg. of chromium or to 0.01 per cent of chromium in a 1-gram sample, is very small, it seemed worth while to investigate it further to see if it was constant with steels of varying chromium content so that a correction could be applied for it, and to try to explain the reason for it.

Samples of Bureau of Standards steel 50 (*a*), containing 3.52 per cent of chromium and 0.976 per cent of vanadium, were weighed out: samples 1 to 3 = 0.6 gram, 4 to 6 = 0.8 gram, 7 to 9 = 1 gram, 10 to 12 = 1.0 gram to which 10 cc. of 0.05040 *N* potassium dichromate were added, and 13 to 15 = 1.0 gram to which 20 cc. of the same dichromate solution were added. These samples were prepared in the same way as those used in Table V. Three-tenths cubic centimeter of 0.01 *M* indicator, oxidized, was added in every case before titration of the chromic and vanadic acids with 0.05 *N* ferrous sulfate, standardized as directed for the experiments in Table V. The results of this series of experiments are given in Table VI.

The average indicator blank in experiments 4 to 15 is −0.30 cc. and the data show that this value is quite independent of the quantity of chromium present. From previous statements one would expect this blank to be −0.15 cc. rather than −0.30 cc. of 0.05 *N* ferrous sulfate.

Duplicate 1-gram samples of Bureau of Standards steels 50 and 50 (*a*) were prepared as for Table V. No indicator solution was added. Forty cubic centimeters of sulfuric acid (specific gravity, 1.5) were added, the solutions cooled to 5° to 6° C. and held at this temperature during electrometric titration with 0.05 *N* ferrous sulfate which had been standardized electrometrically against standard ceric sulfate. A silver chloride–platinum electrode system was used. For steel 50 (*a*), containing 3.52 per cent of chromium, 3.516 and 3.522 per cent were obtained; for 50, containing 3.61 per cent of chromium, 3.611 and 3.607 per cent. The change in potential at the end point was much smaller than for a similar solution without tungstic and hydrofluoric acids, so that the electrometric method for obtaining the end point here can not be recommended. In these titrations equilibrium was reached quite slowly in the region of the end point—an indication, possibly, that in a titration with the indicator slightly more than the theoretical quantity of ferrous sulfate is used before the color change takes place. Some oxidized indicator was added to another solution shortly before the end point was reached in an electrometric titration, to see whether the color change occurred at the electrometric end point. The solution was still purple at that end point and approximately 0.07 cc. more of 0.05 *N* ferrous sulfate was required to produce the change in color. This change was not sharp, however, because of too high acid concentration, so that this experiment while of use qualitatively in showing that the indicator end point occurs after the electrometric, is not of value quantitatively in determining the exact difference between these two end points. It seems probable that this slight error of 0.1 mg. of chromium is caused by a fairly slow reaction at the end point. The error appears always constant in value and is easily included in the blank correction and thus eliminated.

Table VI. Change in Value of Indicator Blank for Chromium Determinations in Tungsten Steels with Change in Per Cent of Chromium Present

Sample	Chromium Present	Chromium Found	Blank in 0.05 *N* $FeSO_4$		Chromium Present after Blank Correction of −0.30 cc. of 0.05 *N* $FeSO_4$
	Gram	*Gram*	*Cc.*		*Gram*
1	0.02112	0.02117	−0.06		
2	0.02112	0.02113	−0.01	−0.04	
3	0.02112	0.02116	−0.05		
4	0.02816	0.02827	−0.13		0.0280
5	0.02816	0.02839	−0.26	−0.23	0.0281
6	0.02816	0.02841	−0.29		0.0281
7	0.0352	0.03551	−0.35		0.0353
8	0.0352	0.03560	−0.45	−0.36	0.0353
9	0.0352	0.03546	−0.29		0.0352
10	0.04394	0.04412	−0.21		0.0439
11	0.04394	0.04412	−0.21	−0.27	0.0439
12	0.04394	0.04427	−0.38		0.0440
13	0.05267	0.05292	−0.29		0.0527
14	0.05267	0.05293	−0.30	−0.32	0.0527
15	0.05267	0.05300	−0.38		0.0527

Oxidized Diphenylamine or Diphenylbenzidine in Determinations of Chromium and Vanadium

Kolthoff and Sarver (*2*) consider the steps in the oxidation of either of these indicators similar to the reactions suggested by them (*4*) for the oxidation of diphenylamine sulfonic acid. Consequently a preliminary oxidation of either indicator causes the value of any blank correction to become negligible (*3*), as the blanks for these two indicators when not oxidized are considerably smaller than the blank for unoxidized diphenylamine sulfonic acid.

One-tenth per cent solutions of diphenylamine and diphenylbenzidine were prepared by dissolving 0.1 gram of the indicator in 10 cc. of sulfuric acid (specific gravity, 1.83) and diluting this solution with 90 cc. of glacial acetic acid. The method of preparing portions of oxidized indicator solution from these 0.1 per cent solutions was the same as used for diphenylamine sulfonic acid, except that 5 cc. of phosphoric acid (specific gravity, 1.37) instead of water were added to a measured volume of the indicator in a very small beaker. No sulfuric acid was added, but only 3 or 4 drops of dichromate, followed by very dilute ferrous sulfate. The oxidized diphenylamine solution was always clear, while with diphenylbenzidine, probably because of its much smaller solubility, the solution of the oxidized compound was not always clear nor was the color development of solutions to which it was added always good. Since diphenylamine is less expensive and more available, it was used in all further experiments.

Five-gram samples of ingot iron were treated with potassium dichromate solution equivalent to 35 mg. of chromium, ammonium vanadate solution equivalent to 10 mg. of vanadium, and 10 cc. of sulfuric acid (specific gravity, 1.83). The permanganate-azide method for vanadium in a chrome-vanadium steel was followed (*7*). To two of the samples 0.6 cc. of 0.1 per cent unoxidized diphenylbenzidine was added and after 5 minutes the solutions were titrated with 0.025 *N* ferrous sulfate. The volumes required were 7.97 and 7.93 cc., which, after the necessary indicator correction of 0.03 cc. of 0.025 *N* ferrous sulfate per 0.1 cc. of indicator used (*8*), become 8.15 and 8.11 cc. Two more samples of vanadic acid were treated with 0.3 cc. of 0.1 per cent diphenylamine, which had been oxidized, and allowed to stand for 5 minutes. The volumes of ferrous sulfate required were 8.12 and 8.13 cc.

Experiments in which measured portions of a solution of potassium dichromate were titrated with 0.025 *N* ferrous sulfate, after the addition of phosphoric acid, water, and indicator, showed that the usual blank required for diphenylamine disappeared in these cases, as in vanadic acid titrations, when the oxidized indicator was used. Results for chromium and vanadium in chrome-vanadium steels, using oxidized diphenylamine as indicator, are given in the following paper. It was not found possible to make up a stable stock solution of oxidized diphenylamine, as was done with the sulfonic acid derivative.

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New Procedures for Chromium and Vanadium in Alloy Steels

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In chromium or vanadium determinations in tungsten steels the tungsten is kept in solution throughout the analysis as a complex fluoride. The excess of permanganate used in the oxidation of vanadyl ion in vanadium determinations or formed during a persulfate oxidation of vanadium and chromium may be reduced either by sodium azide, followed by boiling to remove hydrazoic acid, or by sodium nitrite at room temperature, followed by urea to destroy excess nitrite.

In such steels oxidized diphenylamine sulfonic acid is used as internal indicator in the titration of vanadic or chromic acids with ferrous sulfate. By this preliminary oxidation of the indicator the blank is reduced to a very small value, and is sufficiently constant with definite procedures to be eliminated by the proper correction. The usual direct method for chromium with addition of excess standard ferrous sulfate and back-titration with standard permanganate is applicable. These procedures for vanadium and chromium in steels containing tungsten are accurate and more rapid than those now in use.

These same reducing agents have been applied to vanadium and chromium determinations in steels without tungsten, thereby shortening the procedures now used. In these cases oxidized diphenylamine may be used as the internal indicator for the titrations with ferrous sulfate. By the use of this oxidized indicator both in the analysis and in the standardization of the ferrous sulfate, any blank correction for the indicator is eliminated.

While rapid and accurate indicator methods are available for chromium and vanadium in chrome-vanadium steels, there is at present but one indicator method for either element in tungsten steels which does not involve the removal of the tungsten, and that is for vanadium (*5*). A separation of tungsten is undesirable, both because of the time required and also because the precipitated tungstic acid always contains traces of vanadium and sometimes of chromium which have to be determined separately. The chromium in the precipitated tungstic acid is much more easily determined than the vanadium, but good methods for the latter are of greater importance, since it is always present in the precipitate.

In this method for vanadium the tungsten is kept in solution as a complex fluoride (*5*), and diphenylamine sulfonic acid is used as indicator. The blank required for the latter is undesirably large, but the authors, in a recent detailed study of the behavior of this indicator in chromic and in vanadic acid solutions (*6*), have shown that the blank may be greatly reduced by a preliminary oxidation of the indicator, and they have worked out the values for blanks when definite procedures are followed.

The permanganate-azide method for vanadium (*5*) makes use of sodium azide to destroy the excess of permanganate after the oxidation of the vanadyl salt, the excess of hydrazoic acid being destroyed by boiling. Lang and Kurtz (*1*) used sodium nitrite instead of azide for this purpose, followed by urea to destroy excess of nitrite, but they did not show the possible variation in conditions with this reducing agent. The authors have investigated this matter and have found that nitrite and urea may be used very satisfactorily under conditions requiring less time than those suggested by Lang and Kurtz. The substitution of nitrite and urea for sodium azide shortens the method for vanadium, as it is unnecessary

in the former case to boil the solution for a few minutes to remove the excess of reducing agent.

It has been found possible, also, to use the persulfate oxidation method for chromium and vanadium while keeping the tungstic acid in solution as a complex fluoride. The excess of persulfate is destroyed by boiling, and the permanganate formed may be reduced in one of three ways: by the usual procedure employing 1 to 3 hydrochloric acid, followed by a 10-minute period of boiling to remove all chloride; by sodium azide added in slight excess to the boiling hot solution, which is boiled a minute or two to remove all hydrazoic acid; or, by sodium nitrite added in slight excess to the boiling hot solution or to the solution at room temperature, followed at once by urea to destroy all excess nitrite.

The conditions under which sodium azide or sodium nitrite and urea may be used to destroy the excess of permanganate in vanadium or in chromium determinations are given below and from the analytical results obtained and the procedures recommended it will be seen that the methods suggested for these two elements, especially in tungsten steels, are not only accurate but also more rapid than any others.

Method of Destroying Excess Permanganate in Determination of Vanadium

To determine the conditions under which sodium nitrite may be used to destroy the excess of permanganate in vanadium determinations, 1-gram samples of a chrome-vanadium-tungsten steel containing 0.994 per cent of vanadium were taken, and the procedure for the permanganate-azide method followed through the oxidation of vanadyl salt with permanganate at room temperature, with the one exception that after decomposing the steel with sulfuric acid the hydrofluoric acid was added before any nitric acid. With this modification it was found that no trace of tungstic acid ever precipitated, a difficulty which was encountered occasionally when some nitric acid was added before the hydrofluoric acid. To the solution containing vanadic and permanganic acids, 175 to 200 cc. in volume, 0.05 *M* sodium nitrite was added drop by drop from a buret until the permanganate color had disappeared. Then the excess of sodium nitrite indicated in Table I was added, followed by a definite quantity of urea. Air was bubbled through the solution for the stated time or else the solution was allowed to stand for a time before the addition of 3 cc. of hydrofluoric acid (48 per cent) and 0.3 cc. of 0.01 *M* diphenylamine sodium sulfonate, oxidized. The vanadic acid was then titrated with 0.025 *N* ferrous sulfate standardized against pure dichromate by the procedure recommended below. An indicator blank of +0.05 cc. of 0.025 *N* ferrous sulfate was applied in each determination (*6*). The results are given in Table I.

Table I. Use of Sodium Nitrite with Urea to Destroy Permanganate after Oxidation of Vanadium

Excess of 0.05 *M* $NaNO_2$	Urea	Time Air Bubbled through Soln.	Time Soln. Allowed to Stand	Vanadium
Cc.	*Grams*	*Min.*	*Min.*	%
1	1	1	0	1.003, 1.008
1	1	10	0	1.001
5	1	5	0	0.999, 0.986
10	1	5	0	0.990
1	5	5	0	0.993
5	5	15	0	0.986
5[a]	1	5	0	1.003
1	1	0	0	1.011. 1.011
5	1	0	0	1.000, 1.003
5	5	0	15	0.991. 0.990
5	1	0	15	0.997, 0.995
5	1	0	10	0.995, 0.993
5	1	0	5	1.003, 0.993
5	2	0	5	0.990, 0.995
1	2	0	5	0.994, 1.006

[a] The solution containing the 5 cc. excess nitrite was allowed to stand for 5 minutes before the urea was added.

Quantitative results are obtained with a considerable variation in quantities of reagents used and experimental procedure. By bubbling air through the solution, any oxides of nitrogen formed are removed. Their presence in the solution causes no harm, however, as the later experiments in the table show. The reason for the slightly lower results when air is bubbled through the solution, larger quantities of urea are used, or the solution containing the urea is allowed to stand for a few minutes is not clear unless a certain time is required for the last traces of nitrite to be acted on by urea. The 15-minute period of standing, recommended by Lang and Kurtz (*1*), is unnecessary, as Table I shows.

Samples of Bureau of Standards steel 50 (*a*), containing 0.976 per cent of vanadium, to which this permanganate-nitrite-urea method was applied gave 0.977, 0.975, and 0.982 per cent of vanadium, and samples of Bureau of Standards steel 50, containing 0.756 per cent of vanadium, gave 0.756, 0.760, and 0.756 per cent of vanadium.

The conditions under which quantitative results are obtained, using sodium azide instead of sodium nitrite and urea to destroy permanganate, have already been described (*5*).

Method of Destroying Permanganate after Persulfate Oxidation in Determinations of Chromium

One-gram samples of a chrome-vanadium-tungsten steel containing 4.36 per cent of chromium and 0.994 per cent of vanadium were treated with water and sulfuric acid. After the steel was decomposed, hydrofluoric acid was added, followed by nitric acid, and the solution was boiled a short time to remove oxides of nitrogen. After dilution to 300 cc., the solution was heated, silver nitrate and ammonium persulfate were added, and the solution was boiled for 10 minutes to destroy all persulfate. Either of two procedures was used to reduce the permanganate formed. In one method, 0.1 *M* sodium azide was added, drop by drop, to the solution at boiling temperature until the permanganate color had disappeared. Then the excess azide indicated in Table II was added and the solution, after being boiled for a specified period to remove hydrazoic acid, was cooled to room temperature. In the other method, 0.05 *M* sodium nitrite was added in the same manner, followed at once by 1 gram of urea, and the solution was cooled to room temperature. To the 300 cc. of solution obtained by either method, 3 cc. of hydrofluoric acid and 0.3 cc. of 0.01 *M* diphenylamine sodium sulfonate, oxidized, were added, and the chromic and vanadic acids titrated with 0.05 *N* ferrous sulfate standardized against pure dichromate by the procedure recommended below. An indicator blank of −0.30 cc. of 0.05 *N* ferrous sulfate was applied in each determination (*6*). The results are given in Table II.

Table II. Use of Sodium Azide or Sodium Nitrite with Urea to Destroy Permanganate after Persulfate Oxidation of Chromium and Vanadium

Excess NaN_3, 0.1 *M* Added at 95–100° C.	Time of Boiling to Remove HN_3	Cr from Cr + V Titration	Excess $NaNO_2$, 0.05 *M* Added at 95–100° C.	Time of Boiling to Remove Oxides of N	Cr from Cr + V Titration
Drops	*Min.*	%	*Drops*	*Min.*	%
1–2	0	4.38	1–2	0	4.36
1–2	1	4.36	1–2	1	4.38
1–2	5	4.37	1–2	5	4.35
Cc.			*Cc.*		
0.5	5	4.34	0.5	5	4.31
			0.5	0	4.37
1	5	4.35	1	5	4.31
1	3	4.37	1	0	4.33
5	5	4.32			
			1 (at 25° C.)	0	4.35
			3 (at 25° C.)	0	4.32

Because of previous work done by the authors in which sodium azide was found to reduce ceric sulfate selectively in an acid solution containing chromic acid (*7*), no difficulty was anticipated in its use to reduce permanganic acid in the presence of chromic acid. At 95° to 100° C. the reaction between

Table III. Chromium from Chromium Plus Vanadium Determinations

Steel		Agent Used to Destroy Permanganate after Persulfate Oxidation: 1:3 HCl	0.1 M NaN_3	0.05 M $NaNO_2$ + Urea
B. S. 50	(Cr = 3.61%; V = 0.756%; W = 17.56%)	3.59, 3.60, 3.59	3.62, 3.60, 3.61	3.61, 3.60, 3.60
B. S. 50(*a*)	(Cr = 3.52%; V = 0.976%; W = 18.25%)	3.52, 3.51, 3.52	3.52, 3.51, 3.52	3.52, 3.53, 3.53
1[a]	(Cr = 4.10%; V = 1.82%; W = 14.3%)	.....	4.11, 4.09, 4.10	4.11, 4.11, 4.10
2[a]	(Cr = 2.83%; V = 0.473%; W = 15.6%)	.....	2.82, 2.82, 2.82	2.80, 2.84, 2.83

[a] The chromium and vanadium in these steels were determined by methods developed by the authors (*3*, *4*).

Table IV. Vanadium and Chromium Determinations in Steels without Tungsten

(Oxidized diphenylamine as indicator, no indicator correction applied)

Steel		Vanadium	Chromium: Persulfate method	Chromium: Permanganate method
		%	%	%
B. S. 30(*a*)	(V = 0.20%; Cr = 1.02%)	0.203, 0.202, 0.201[a]	1.02,[a] 1.02,[b] 1.04[c]	1.03, 1.03, 1.04,[a] 1.02[a]
B. S. 30(*c*)	(V = 0.235%; Cr = 0.977%)	0.236, 0.236, 0.238[b]	0.974,[b] 0.974[c]	0.970, 0.969, 0.965[a] 0.970[a]
B. S. 32(*b*)	(V = 0.006%; Cr = 0.638%; Ni = 1.21%)	.....	0.629, 0.633, 0.634[b]	0.658, 0.633, 0.633,[a] 0.642[a]
B. S. 73	(V = 0.034%; Cr = 13.93%)	.....	13.91, 13.89, 13.90, 13.93[a] 13.96, 13.89, 13.85, 13.94[b]	.....
B. S. 101	(V = 0.044%; Cr = 17.54%; Ni = 8.44%)	.....	17.61, 17.57, 17.63[a] 17.57, 17.57, 17.57[b]	17.54, 17.42, 17.44,[a] 17.46[a]

[a] Sodium azide used as reducing agent for permanganic acid.
[b] Sodium nitrite used as reducing agent for permanganic acid.
[c] 1:1 hydrochloric acid used as reducing agent for permanganic acid.

permanganic and hydrazoic acids is very rapid, and it is easy to gage the necessary quantity of the latter within a drop or two. With only a drop or two excess of azide, the indicator color can be developed without boiling the solution, but in order to use a constant indicator blank it is probably better to remove all hydrazoic acid by boiling for 1 or 2 minutes. The reaction between permanganic and nitrous acids at 95° to 100° C. is also very rapid and it is equally easy here to avoid the use of more than one or two drops excess. After the addition of urea it is not necessary to boil this solution. Though chromic acid is somewhat more sensitive to a considerable excess of nitrous acid than to the same excess of hydrazoic acid in hot solution, as Table II indicates, the two reducing agents are equally satisfactory when limited to a few drops in excess.

One-gram samples of four different steels were analyzed for chromium plus vanadium, using the procedures just described. With the per cent of vanadium known, the per cent of chromium was calculated. Results are recorded in Table III.

Though the three methods for destroying permanganate after a persulfate oxidation are equally accurate, the time for an analysis is shortened by using azide or nitrite and urea instead of hydrochloric acid. Also, with these new reducing agents no silver chloride is precipitated, and the color change in the clear solutions is very sharp.

Experiments in which permanganate (*2*) was substituted for persulfate in the oxidation of chromium and vanadium in tungsten steels and the excess of permanganate destroyed with sodium azide were not quantitative. No manganese dioxide was formed, but, because of the fluoride ion in these solutions, manganese was undoubtedly present in the trivalent form, so that it was impossible to gage correctly the amount of azide to be added.

Recommended Procedure for Vanadium in Tungsten Steels

Add 25 to 30 cc. of water and 5 cc. of sulfuric acid (specific gravity, 1.83) to a 1-gram sample of the steel weighed into a 400-cc. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Rub loose from the beaker all tungsten and to the boiling hot solution add 5 cc. of hydrofluoric acid (48 per cent), then nitric acid (specific gravity, 1.42), at first slowly, using 5 cc. in all. Boil 2 minutes. A clear green solution is obtained. If the solution is not perfectly clear at this point, as occasionally happens with steels especially difficult to decompose, boil 2 or 3 minutes longer. Dilute to approximately 100 cc., add 1 gram of ammonium persulfate, and boil 5 minutes. Add 5 cc. of 0.1 N ferrous sulfate, dilute to between 175 and 200 cc., and cool to room temperature. Add to this solution 0.1 N potassium permanganate from a buret until a distinct color persists for 2 minutes, to be sure all the vanadium is oxidized. At this point either procedure *A* or *B* may be used. The authors prefer procedure *A*.

A. Add 0.05 M sodium nitrite slowly from a buret until the solution becomes green, then 5 cc. excess of the nitrite solution, followed by 2 grams of urea. Stir the solution thoroughly and allow it to stand for 5 minutes.

B. Add 5 cc. of 0.1 M sodium azide and boil vigorously (in hood) for 5 minutes to remove all the hydrazoic acid. Cool to room temperature.

To the solution thus obtained add 3 cc. of hydrofluoric acid (48 per cent) and 0.3 cc. of 0.01 M diphenylamine sodium sulfonate which has been oxidized (*6*), and titrate at once with 0.025 N ferrous sulfate standardized as directed below. The color change of the indicator at the end point is from purple to green. The correction to be applied for the indicator may be determined from the following table and should be subtracted from or added to the volume of ferrous sulfate used in the titration (*6*).

Vanadium in Steel	Indicator Corrections in 0.025 N $FeSO_4$
%	Cc.
0–0.85	−0.10
0.85–1.2	+0.05
1.2–3.5	+0.10

Standardization of Ferrous Sulfate Solution for Vanadium Determinations. Weigh out 0.04- to 0.06-gram samples of pure potassium dichromate into 400-cc. beakers and dissolve in a little water, or measure out that volume of standard dichromate solution which will require 35 to 50 cc. of 0.025 N ferrous sulfate for titration. Add 5 cc. of sulfuric acid (specific gravity, 1.5), 5 cc. of phosphoric acid (specific gravity, 1.37), and dilute to 200 cc. Then add 0.3 cc. of 0.01 M indicator, oxidized, and titrate with approximately 0.025 N ferrous sulfate. No blank correction is required in this standardization (*6*).

Recommended Procedure for Chromium Plus Vanadium in Tungsten Steels

Add 25 to 30 cc. of water and 5 cc. of sulfuric acid (specific gravity, 1.83) to a 1-gram sample of the steel weighed into a 600-cc. beaker. Warm gently until the steel is completely decomposed and the tungsten separates out as a black powder. Rub loose from the beaker all tungsten and to the boiling hot solution add 5 cc. of hydrofluoric acid (48 per cent), then nitric acid (specific gravity, 1.42), at first slowly, using 5 cc. in all. Boil 2 minutes. A clear green solu-

tion is obtained. If the solution is not perfectly clear at this point, as occasionally happens with steels especially difficult to decompose, boil 2 or 3 minutes longer. Dilute to approximately 300 cc., heat to 60° C. or higher, add 10 cc. of silver nitrate solution (2.5 grams of silver nitrate per liter), 5 grams of ammonium persulfate, and boil vigorously for 10 minutes. A few small pieces of broken porcelain in the solution will prevent bumping. Any one of the three following procedures may be used to destroy the permanganic acid formed during the oxidation process. The authors prefer procedure *A*.

A. Add 0.1 *M* sodium azide, drop by drop, from a pipet to the boiling hot solution until all permanganate has been reduced, limiting the excess of azide used to 1 or 2 drops. Boil for 1 or 2 minutes to remove the hydrazoic acid.

B. Add 0.05 *M* sodium nitrite, drop by drop, from a pipet to the boiling hot solution until all permanganate has been reduced, limiting the excess of nitrite used to 1 or 2 drops. Then add 1 gram of urea at once and stir the solution thoroughly.

C. Add 5 cc. of 1 to 3 hydrochloric acid to the hot solution and boil vigorously for 10 minutes to reduce the permanganate and remove all chlorine.

To the solution from *A*, *B*, or *C*, cooled to room temperature, add 3 cc. of hydrofluoric acid (48 per cent) and 0.3 cc. of 0.01 *M* diphenylamine sodium sulfonate, oxidized (*6*), and titrate at once with 0.05 *N* ferrous sulfate standardized as directed below. Immediately after the addition of the indicator the solution is a yellowish brown. As the ferrous sulfate is added this yellow color disappears gradually, being replaced first by a purplish red and then by a clear purple. The color change at the end point from purple to green is very sharp. An indicator blank of −0.30 cc. of 0.05 *N* ferrous sulfate should be applied to the volume of ferrous sulfate used in the titration (*6*).

Standardization of Ferrous Sulfate for Chromium Plus Vanadium Determinations. Place in a 600-cc. beaker that amount of potassium dichromate, either in solid form dissolved in a little water or in the form of a standard solution, which will require approximately 35 to 50 cc. of 0.05 *N* ferrous sulfate. Add 5 cc. of sulfuric acid (specific gravity, 1.5), 5 cc. of phosphoric acid (specific gravity, 1.37), and dilute to 300 cc. Then add 0.3 cc. of 0.01 *M* indicator, oxidized, and titrate with approximately 0.05 *N* ferrous sulfate. No blank correction for the indicator is required here (*6*).

Direct Determination of Chromium in Steels Containing Tungsten

Experiments were carried out to determine whether the direct method for chromium in chrome-vanadium steels—that is, persulfate oxidation followed by the addition of excess standard ferrous sulfate and back-titration of the excess reducing agent and vanadyl sulfate with standard permanganate—could be applied to steels in which the tungstic acid was held in solution as a complex fluoride. The persulfate method as described above was used with 1-gram samples of a chrome-vanadium-tungsten steel. Sodium azide, one or two drops in excess, was added to the boiling hot solution to destroy the permanganate formed during the oxidation, and the solution was boiled 1 or 2 minutes to remove all hydrazoic acid. To one sample, cooled to room temperature, an excess of 0.1 *N* ferrous sulfate was added, and the solution titrated at once with 0.02 *N* potassium permanganate. Though this solution containing fluoride has very little color, it was found more difficult to obtain an accurate end point with permanganate than in solutions of steels without tungsten. It was thought that the fluoride ion might be responsible for this difficulty. Ten grams of boric acid were added to another sample of the steel just before the addition of excess standard ferrous sulfate. During the titration with standard permanganate this solution was more green in color than the fluoride solution in the first experiment. The end point with permanganate did not appear, however, to be more distinct in this solution than in the other. The steel contained 4.36 per cent of chromium; 4.31 per cent was obtained for the first sample above and 4.32 per cent for the second with no blank correction made for color interference at the end point. A number of analyses, in which both methods suggested above were tested with conditions varied somewhat, indicated that this direct method for chromium was possible in the hands of an operator trained to recognize the permanganate end point. Though not as exact a method as the one already described for chromium plus vanadium, it is rapid and can be made sufficiently accurate by applying proper blank corrections for the color at the end point.

Oxidized Diphenylamine as Indicator for Vanadium or Chromium Plus Vanadium in Steels without Tungsten

The elimination of the indicator blank by a preliminary oxidation of diphenylamine has already been discussed (*6*). Obviously such an indicator is of value in vanadium or chromium determinations in steels free from tungsten, but is useless in steels containing it. Results of a number of analyses are given in Table IV, in all of which oxidized diphenylamine was used as indicator. The recommended procedures for such analyses are given later.

Five-gram samples were used for the vanadium determinations. The authors recommend the use of sodium nitrite as reducing agent, as the results are just as accurate as with sodium azide and the method is more rapid.

Two-gram samples were used in the chromium determinations by the persulfate method with the exception of Nos. 73 and 101, 0.25-gram samples of which were used. Table IV shows that accurate results were obtained for chromium with azide, with nitrite and urea, or with hydrochloric acid as reducing agent for the permanganic acid after a persulfate oxidation. With the stainless steel, No. 73, however, when sodium azide was added in slight excess to the boiling hot solution and the solution boiled 1 or 2 minutes to remove hydrazoic acid, a reddish color developed in some samples during the period of boiling. When sodium nitrite was added in slight excess to the boiling hot solution of this stainless steel, followed at once by urea, it was necessary to boil this solution for 5 minutes before cooling and continuing the analysis. Without this period of boiling, a deep blue color kept reappearing in the solution after the end point had apparently been reached in the ferrous sulfate titration and it was impossible to carry out a rapid titration to a permanent green color. During the period of boiling, after the addition of nitrite and urea, the solution in many cases became a deep orange in color. The cause of this is not certain, but the color change of the indicator at the end point is just as sharp with such solutions. When 1 to 1 hydrochloric acid was used as the reducing agent for this stainless steel, the results were not quantitative, being invariably about 0.1 per cent low. The authors prefer sodium azide as the reducing agent after a persulfate oxidation because chromic acid in a hot solution is less sensitive to it than to nitrite and also because the azide offers a shorter procedure than that in which hydrochloric acid is used.

The possibility of using sodium azide to destroy all permanganate and thus avoiding a filtration in the permanganate method for chromium plus vanadium in steels without tungsten (*2*) was tested. Even at the boiling temperature the reaction between azide and the manganese dioxide formed in this method was rather slow, and if considerable precipitate was present it was difficult to limit the excess of azide to a small amount. When nitrite with urea was used as the reduc-

ing agent, results were low. If, however, phosphoric acid was present at the time the permanganate was added, and if the solution containing a moderate excess of permanganate was boiled for 2 minutes before addition of azide, the oxidation of the chromium and vanadium was quantitative and only a small amount or in some cases no manganese dioxide was formed. The procedure given later in this paper for chromium plus vanadium in steels without tungsten was used in dissolving samples and oxidizing carbonaceous material and ferrous salts. Such a solution, 300 cc. in volume, and containing phosphoric acid, was heated to boiling, a 2 per cent permanganate solution added until a deep purple color remained, the solution boiled 2 minutes, and then 0.1 *M* sodium azide added slowly to the boiling hot solution until a few drops excess were present. It is very important that the solution be boiling hot during the addition of azide, especially if any manganese dioxide is present. The azide will destroy the permanganate color first. Then further azide should be added slowly, drop by drop, until the solution clears. The solution was boiled for 5 minutes to remove all hydrazoic acid. From this point the procedure already referred to was followed. The results of analyses of 2-gram samples of Bureau of Standards steels 30 (*a*), 30 (*c*), and 32 (*b*), and of 0.3-gram samples of 101 are given in the last column in Table IV. Though these analyses are not quite as accurate as those with the persulfate method, the use of permanganate shortens the procedure and gives results of sufficient accuracy for many purposes. Obviously, after the removal of hydrazoic acid by boiling, the chromium can be determined directly by addition of excess standard ferrous sulfate and back-titration with standard permanganate.

Recommended Procedure for Vanadium in Steels without Tungsten

Add 30 to 40 cc. of water to a 4- or 5-gram sample in a 600-cc. beaker. Run in a measured volume of sulfuric acid (specific gravity, 1.83) from a buret, allowing 1.5 cc. for each gram of steel and 3 cc. in excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 30 to 40 cc. of water and heat until the salts have dissolved. To the boiling hot solution add nitric acid (specific gravity, 1.42) in small portions until the oxidation of ferrous sulfate is complete (3 to 3.5 cc. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen, cool to room temperature, add 25 cc. of phosphoric acid (specific gravity, 1.37), and dilute to 300 cc. Add 0.1 *N* potassium permanganate from a buret until an excess is present. Then add 3 or 4 drops more and let the solution stand for 2 minutes to be sure that the color persists and all of the vanadium is oxidized. Either procedure *A* or *B* may be used to destroy excess permanganate. The authors prefer procedure *A*.

A. Add 0.05 *M* sodium nitrite slowly from a buret until the solution becomes green, then 5 cc. excess of the nitrite solution, followed by 2 grams of urea. Stir the solution thoroughly and allow it to stand for 5 minutes.

B. Add 5 cc. of 0.1 *M* sodium azide and boil vigorously (in hood) for 5 minutes to remove all hydrazoic acid. Cool to room temperature.

To the solution thus obtained, add 15 grams of crystallized sodium acetate. This should be the correct amount of acetate to react with the 3 cc. excess of sulfuric acid used in dissolving the steel and with the slight amount of nitric acid present. If too much acetate is added so that a permanent precipitate forms, a drop or two of sulfuric acid will cause the solution to clear. As soon as the acetate has dissolved, add 0.5 cc. of 0.1 per cent diphenylamine (*6*), oxidized, and titrate with 0.025 *N* ferrous sulfate standardized by the method given below.

Standardization of Ferrous Sulfate Solution for Vanadium Determinations

Use sufficient standard potassium dichromate solution to require 35 to 50 cc. of 0.025 *N* ferrous sulfate. Dilute to 300 cc., add 0.5 cc. of 0.1 per cent diphenylamine, oxidized, and titrate with the 0.025 *N* ferrous sulfate.

Recommended Procedure for Chromium Plus Vanadium in Steels without Tungsten

Use a sample of suitable size, varying from 2 grams with low chromium to 0.25 gram with stainless steels. Place it in a 600-cc. beaker, add 15 cc. of water, 15 cc. of phosphoric acid (specific gravity, 1.37), and run in a measured volume of sulfuric acid (specific gravity, 1.83) from a buret. Allow 1.5 cc. of acid for each gram of steel and 3 cc. excess. After the steel has been completely decomposed, boil until a considerable quantity of salts separates out, in order to assist in decomposing carbides. Dilute with 20 cc. of water and heat until the salts have dissolved. Add nitric acid (specific gravity, 1.42) in small portions to the hot liquid until the violent oxidation of ferrous sulfate is over (2 to 3 cc. of acid are sufficient). Avoid any appreciable excess. Boil the solution to destroy oxides of nitrogen, dilute to 300 cc., heat to boiling and add 10 cc. of silver nitrate containing 2.5 grams of silver nitrate per liter, and 1.5 grams of ammonium persulfate. If no permanganate tinge appears in the solution on boiling, add more ammonium persulfate. In no case will more than 2 to 2.5 grams be required if samples of the weights suggested above are used. Boil the solution for 10 minutes to decompose the excess persulfate, and use either procedure *A* or *B* to reduce the permanganate formed. The authors prefer procedure *A*.

A. Add 0.1 *M* sodium azide, drop by drop, from a pipet to the boiling hot solution until all permanganate has been reduced, limiting the excess of azide added to 2 or 3 drops. Boil for 2 minutes to remove the hydrazoic acid. A reddish color which may develop in the solution during the boiling period may be disregarded.

B. Add 0.05 *M* sodium nitrite, drop by drop, from a pipet to the boiling hot solution until all permanganate has been reduced, limiting the excess used to 2 or 3 drops. Then add 1 gram of urea at once and boil the solution for 5 minutes. A reddish color which may develop in the solution during the boiling period may be disregarded.

To the solution from *A* or *B*, cooled to room temperature, add that quantity of crystallized sodium acetate which is required to react with the excess of sulfuric acid used in dissolving the steel (1 cc. of concentrated sulfuric acid is equivalent to 4.8 grams of sodium acetate trihydrate). As soon as this has dissolved, add 0.5 cc. of 0.1 per cent diphenylamine, oxidized, and titrate with 0.05 *N* ferrous sulfate. The ferrous sulfate should be standardized by the procedure given under vanadium in steels without tungsten. That volume of standard dichromate should be taken which will require about 35 to 50 cc. of ferrous sulfate.

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Determination of Potassium by Sodium Cobaltinitrite

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VARIOUS methods have been proposed from time to time for the determination of small amounts of potassium by the use of sodium cobaltinitrite. Although many workers have reported their methods as rapid, economical, and accurate, none seems to have been extensively used, probably because of unsatisfactory results. Since good and poor results obtained by the same methods have been reported by various workers, it was thought that perhaps certain steps or points in the procedure had been overlooked or insufficiently evaluated. A study of all the factors which it was thought could influence the recovery of potassium was made, and this paper presents an outline of the procedure evolved from this study with certain valuable points in technic.

After a review of procedures proposed for the use of sodium cobaltinitrite, the method given by Peng (*5*) was selected as a basis for this work, as being most satisfactory and suitable for existing conditions. A large number of potassium determinations on known and unknown solutions under varying conditions were made, and the following procedure was evolved. Its advantages are primarily in the temperature of precipitation, the precipitating medium, the time of precipitation, the washing of the precipitate, and the titration. It has given excellent results for many workers on different kinds of extracts and water solutions of potassium during the last two years.

Procedure

Place in a 250-ml. beaker a 25-ml. or less aliquot of the unknown potassium solution. Make just alkaline to phenolphthalein with sodium hydroxide and add 4 drops of acetic acid. After adding 10 ml. of 95 per cent ethyl alcohol, bring total volume of solution to 35 ml. Cool this solution to 5° to 6° C. and then add 5 ml. of a similarly cooled sodium cobaltinitrite solution slowly down the sides of the beaker with shaking. After the precipitate and solution have stood overnight at 5° to 6° C., filter on a freshly prepared asbestos pad and wash beaker and pad thoroughly with the cold wash solution. Usually 10 to 20 washings of 5 to 10 ml. each will be sufficient. After completing the washing, transfer the pad and precipitate to the original beaker with a stream of hot water. If a Hirsch funnel, which is very convenient, is used to retain the asbestos, it is necessary to pour the water through it to rinse out the inside. Bring the content of the beaker to about 150 ml. with the hot water and titrate immediately with standard potassium permanganate. Simultaneously with the starting of titration add from 5 to 10 ml. of concentrated nitric acid with rapid stirring. Always keep an excess of permanganate present until nearing the end point. The pink color should remain for about 1 minute. With this end point 1 ml. of a 0.1 *N* potassium permanganate solution is equivalent to 0.0005672 gram of potassium.

Discussion

The manner in which the procedure is carried out is important. The proper preparation of the different solutions is also essential.

It was found that the conditions under which precipitation was made influenced considerably the recovery of potassium. As the method of Peng (*5*) recommended lower temperatures of precipitation than other methods, a number of determinations were made at various temperatures. Low temperatures gave a much better recovery of potassium, 5° C. being best, with very little difference between 5° and 8° C. Temperature also affected the amount of alcohol required for complete precipitation of the potassium. It was possible to bring about almost complete precipitation at 6° C. without any alcohol, but the crystals were too fine to be retained in filtration. The size of the crystals increased as the amounts of alcohol increased. A 25 per cent alcoholic solution (by volume) gave crystals of sufficient size to be retained easily on the filter and not large enough to cause excessive occlusion. The temperature of the precipitating (sodium cobaltinitrite) and potassium solutions at the time of combining affected the recovery. When the solutions were mixed at room temperature the amount regained was low, probably because of the formation of small crystals and subsequent difficulty in filtering. No such difficulty was experienced when the solutions had been previously cooled to 6° C.

Table I. Titration Value and Potassium Recovered from Known Potassium Solution

Sample	Temperature of Precipitation	Potassium in Solution	0.1 *N* $KMnO_4$ Required	Potassium Recovered
	° C.	*Mg.*	*Ml.*	*Mg.*
1	Room	5.0	6.98	3.96
2	Room	5.0	7.13	4.04
3	Room	5.0	8.09	4.59
4	Room	5.0	7.89	4.47
5	Room	5.0	8.14	4.62
6	Room	5.0	8.09	4.59
7	Room	5.0	8.09	4.59
8	Room	5.0	8.22	4.70
9	Room	5.0	8.19	4.64
10	Room	10.0	15.97	9.06
11	Room	10.0	15.97	9.06
12	6	5.0	8.80	4.99
13	6	5.0	8.85	5.02
14	6	5.0	8.83	5.01

Table II. Effect of Acidity and Alkalinity upon Recovery of Potassium from Standard Potassium Chloride Solution (Precipitated at 6° C.)

Concd. HCl Added to K Solution	0.1 *N* $KMnO_4$ Required	Potassium Recovered	10% NaOH Added to K Solution	0.1 *N* $KMnO_4$ Required	Potassium Recovered
Drops	*Ml.*	*Mg.*	*Drops*	*Ml.*	*Mg.*
1	8.74	4.96	1	8.90	5.05
1	8.80	4.99	1	8.95	5.07
1	8.85	5.02	1	8.49	4.82
3	8.44	4.79	3	8.90	5.05
3	8.44	4.79	3	8.90	5.05
3	8.49	4.82	3	9.00	5.10
3	8.44	4.79	5	9.20	5.22
5	8.29	4.70	5	9.15	5.19
5	8.59	4.87	5	9.00	5.10
5	8.44	4.79	5	8.80	4.99
5	8.29	4.70	10	8.90	5.05
7	7.73	4.39	10	9.00	5.10
7	7.89	4.47	10	8.95	5.07
7	8.29	4.70	20	8.69	4.93
10	6.17	3.50	20	8.69	4.93
10	6.62	3.76	20	8.80	4.99
10	7.28	4.13	20	8.75	4.96
10	7.08	4.01	20	8.69	4.93

When the precipitate was permitted to stand for a longer time before filtering the amount of potassium recovered was also greater, as previously noted by Van Rysselberge (*6*). A maximum was reached after the precipitate had stood overnight at 6° C. The reaction of the unknown solution also influenced the recovery of potassium (Table II). Peng controlled this point indirectly and partially when he suggested adding acetic acid until the phenolphthalein color disappeared. In the procedure as outlined the solution is

made slightly acid with acetic acid, which supplies the necessary acetate ion in addition to aiding in the control of the reaction. The stabilizing influence of the acetate ion is shown in Table III. It was found that it could be supplied by a salt as well as by acetic ion, although the latter was preferred as it helped adjust the reaction.

Table III. Effect of Acetate Ion upon Recovery of Potassium (Precipitated at 6° C.)

Acetate Ion Added	0.1 N $KMnO_4$ Required	Potassium Recovered
	Ml.	*Mg.*
None	8.85	5.02
None	8.49	4.82
None	8.64	4.90
None	8.80	4.99
None	8.69	4.93
Acetic Acid		
4 drops	8.80	4.99
4 drops	8.82	5.00
4 drops	8.84	5.02
1 ml.	8.14	4.62
1 ml.	8.39	4.76
1 ml.	8.14	4.62
5 ml.	7.19	4.07
5 ml.	7.89	4.47
5 ml.	7.59	4.30
Sodium Acetate		
0.1 gram	8.80	4.99
0.1 gram	8.84	5.02
0.1 gram	8.77	4.97
2.5 grams	9.10	5.16
2.5 grams	9.05	5.13
2.5 grams	9.15	5.19

Many previous investigators (*1–5*, *7*) had noted the necessity for an excess of sodium over potassium ions, obtained by precipitating in the presence of some sodium salt. In the authors' work sodium cobaltinitrite seemed to give the best results, as is shown in Table III where the large amount of sodium acetate was used. When the amount of sodium cobaltinitrite was less than 150 times that of potassium, low results were obtained. Excessive amounts, up to 1000 times the potassium content, gave satisfactory results. The data in Table IV show the influence of varying the sodium and potassium ion ratio upon the recovery of the potassium.

Table IV. Influence of Varying Ratio of Potassium to Sodium Cobaltinitrite upon Recovery of Potassium (Precipitated at 6° C.)

Potassium Added	Precipitating Reagent Added	0.1 N $KMnO_4$ Required	Potassium Recovered
Mg.	*Ml.*	*Ml.*	*Mg.*
3	5.0	5.15	2.92
3	5.0	5.30	3.01
3	5.0	5.25	2.98
5	2.0	8.15	4.62
5	2.0	8.05	4.57
5	2.0	7.80	4.42
5	2.0	7.90	4.48
5	2.0	7.95	4.51
5	5.0	8.80	4.99
5	5.0	8.84	5.02
5	5.0	8.75	4.96
5	5.0	8.90	5.05
5	5.0	8.80	4.99
5	5.0	8.85	5.02
10	10.0	17.30	9.81
10	10.0	17.70	10.04
10	10.0	17.55	9.96
10	5.0	17.10	9.70
10	5.0	17.00	9.64
10	5.0	16.90	9.59
15	15.0	26.00	14.75
15	15.0	25.55	14.49
15	15.0	25.50	14.46

The sodium cobaltinitrite solution was prepared by dissolving 30 grams in 100 ml. of distilled water. After this solution has cooled at 6° C. for at least an hour it must be filtered through an asbestos pad on a Hirsch funnel similar to that used for filtering the precipitate. It is best to make up this solution fresh when needed.

As the precipitation is made in an alcoholic sodium cobaltinitrite solution, which is oxidized by potassium permanganate, it is necessary that the precipitate be washed free of these substances. If the dipotassium sodium cobaltinitrite precipitate is soluble in the wash solution, some of it may be lost in the numerous washings required. As none of the previous wash solutions proved satisfactory, trials with different wash solutions were made. It was found that distilled water saturated with dipotassium sodium cobaltinitrite and kept at 6° C. was very satisfactory. Washing with this solution removed the alcohol and sodium cobaltinitrite and did not dissolve any detectable amounts of the precipitate.

The solution is prepared by adding a small amount of dipotassium sodium cobaltinitrite or a water suspension of the salt to distilled water previously cooled to 6° C. The water must be cooled before it is saturated with this salt and kept cold afterwards, or the salt decomposes and leaves the wash solution unsatisfactory. The colloidal nature of dipotassium sodium cobaltinitrite makes it difficult to obtain a saturated solution quickly, and it is therefore better to prepare the wash solution a day or two before it is needed. As this salt cannot be conveniently obtained commercially, it was prepared from a potassium chloride and sodium cobaltinitrite solution and purified by decanting. The solution will remain satisfactory for a long time if kept as a water suspension in a dark cool place. Only a few drops of this salt suspension are necessary to prepare a liter of the wash solution.

The asbestos pad and precipitate should be washed into the beaker in which the precipitate was made by means of hot water (preferably water which has just been boiled) immediately upon the completion of the washing. This high temperature gives a sharper end point in titration. It is very desirable to work rapidly from the beginning of filtration until the end of the titration, which normally should not take more than 3 to 4 minutes. It is not necessary to dissolve the precipitate completely before starting the titration, as the stirring in titration will help bring it into solution. The mineral acid added liberates the nitrite rapidly, causing a loss of nitrous acid if the addition of the acid and permanganate is not properly regulated. After a few titrations this can be easily controlled. Either sulfuric or nitric acid can be used, but nitric acid seemed to give a sharper end point. Ordinary c. p. nitric acid was used by the authors, although it should be aërated to remove any nitrous acid that may be present.

It is important for the worker to reach the same end point each time. A blank determination should be run along with some of the other determinations. This is generally from 0.1 to 0.3 ml. of 0.1 N potassium permanganate, depending upon the end point.

Although the end point in titration will vary with the worker, it only slightly affects the potassium equivalent of 1 ml. of 0.1 N potassium permanganate. The variations in values reported by different investigators indicate that the procedure followed will greatly influence this potassium factor. These values were generally lower than the theoretical ones, regardless of the consideration given to the final valence of the cobalt.

This method of titration is different from any other the writers have seen, as other methods require two titrations with permanganate and one with an oxalate solution. The single titration is much preferred as it is simpler, easier, quicker, and just as accurate, if the temperature is high enough and the addition of the acid and permanganate is properly regulated. The factor of 0.0005672 gram of potassium for each milliliter of permanganate required is lower than any other seen. This is believed to result from the length of time the precipitate is allowed to stand before filtering. The equilibrium which is reached may influence the arrangement of the double salt crystals or the amount of occlusion. It is always preferable to check the potassium factor by making some determinations on a known potassium solution, containing somewhere near the same amount of potassium as the unknown.

This method has been found very accurate when the unknown contains between 3 and 10 mg. of potassium, but less than 1 mg. and more than 50 mg. have been satisfactorily determined. For small amounts a 0.05 *N* potassium permanganate solution was used. In the case of large amounts only 0.1 *N* permanganate was used, but it was standardized against a similar amount of known potassium. Ammonium salts have been the only salts which have interfered, because ammonia also forms an insoluble precipitate with sodium cobaltinitrite. Organic matter must not be present in the unknown solution in such a form that it will be occluded in the precipitate or retained on the filter pad. The method is rapid, as one worker can easily make from 20 to 40 determinations a day. By proper precautions the asbestos can be used over and over, and since the sodium cobaltinitrite and alcohol are not exceedingly costly substances the method is not very expensive. This method has been used on many kinds of ash, soil extracts, and total potassium determinations in soils, with very satisfactory results.

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Experimental Determination of Void Content of Close-Packed Mineral Powders

Effect of Particle Size, Shape, and Texture

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In industrial processes the value of a mineral filler depends chiefly on its physical properties, of which the void content is one of the most important. Several commercial mineral powders were divided into five or six definite size fractions and the void contents of the unfractionated powders and the various fractions determined by three methods—dry compaction, liquid absorption, and briquetting. For most of the powders the lowest void content values were obtained by the briquetting method. The data for limestone, silica, marble, and black slate powders indicate that particle size has no appreciable effect on the void content, but the results for trap rock and soapstone apparently do not agree with this generalization. The void content values of the various size fractions of powdered Tripoli and argillaceous silica, minerals which possess peculiar characteristics, are discussed. Although texture has an effect on void content, regularity in particle shape is probably of greater importance.

The fabrication of bituminous, cement, ceramic, paint, plastic, rubber, and numerous other products often requires the use of fine powders. In some processes the particles lose their identity, while in others they retain their original structure and function as fillers, imparting strength, toughness, durability, weight, stability, and weather resistance to the material to which they are added. When a powder is used as a filler its physical properties are usually of primary importance, though adsorption at the solid surface, the adhesion tension between the solid particles and interstitial material, and polymerization caused by surface catalysis may affect to some extent the characteristics of the resulting mixture.

The physical properties of a powder which may affect its value as a filler are the shape, texture, size, and size distribution of the particles, the surface area presented by unit weight or volume of the material, and the percentage of voids in the closely packed dust. Although the significance of these different properties may vary with the material and the purpose for which it is to be used, the void content, bulkiness, or weight per unit volume of the closely packed powder is almost always of importance. Consider, for example, bituminous products which contain high percentages of mineral matter. Other factors being equal, powders which in a close-packed condition possess high void contents raise the softening point, increase the yield value, and in general give greater stability to the mixture than do equal weights of powders with low void contents.

Some theoretical and experimental work has been done on packing and the void contents of powders, sands, and crushed aggregates, but most of the materials used have been coarser and less homogeneous with respect to particle size than the powders with which this paper deals. Norton and Hodgdon (*11*) investigated the void content and particle spacing for a number of clays and "nonplastic" mineral powders. Roller (*13*) compacted dry, carefully size-graded microscopic powders by hand tapping and found that the bulkiness increased with decrease in particle size below 15 to 30 microns in diameter, and Steiner (*14*) obtained the same result with cement. From a study of pigments, Klumpp (*6*, *7*) concluded that liquid absorption depended mainly on the void content of the close-packed powder, and not so much on the size and surface area of the particles as on their shape. Manegold, Hofman, and Solf (*8*, *9*) made an extensive study of the packing of granular materials. The void contents which they calculated for various types of packing of spheres may be of interest.

Points of Contact between Particles	Per Cent Voids
4	66.0
6	47.6
8	39.5
10	30.2
12	25.9

Using a dry compaction method, Westman and Hugill (*15*) found that "particles of uniform shape and size could be packed practically to the same extent over a range of diameters extending from 0.312 to 0.0035 inch." They give results also for the packing of mixtures of various sizes of particles.

Types of Mineral Powders Investigated

The following mineral powders were used in a study of the relation between void content and particle size, shape, texture, etc.

- Limestone
- Silica (99.8 per cent SiO_2)
- Marble (96.0 per cent $CaCO_3$, with remainder chiefly $MgCO_3$)
- Trap rock
- Argillaceous silica
- Soapstone
- Black slate
- Tripoli

All these were commercial products, with the exception of the pure silica and marble which were obtained because it seemed desirable to have materials, the fine fractions of which were of the same mineral as the coarser. At least 90 per cent of each of the powders passed a U. S. Standard No. 200 screen with soapstone, slate, and tripoli almost completely passing through a No. 250 screen.

Data were obtained on the particle size distribution in the powders by means of a laboratory air analyzer similar to that perfected by Roller (*12*). A 25-gram sample of each powder was separated into six fractions and the weight of each determined. Table I indicates the size distribution in the different powders. Because pulverization took place in the apparatus due to the softness of the material, the size distribution in the powdered soapstone was not determined.

Table I. Size Distribution in Powders

Diameter of particles in microns	Weight <2	2–5	5–10	10–20	20–40	40–75	>75
	%	%	%	%	%	%	%
Limestone	8.6	9.0	15.0	15.9	25.0	20.0	6.5
Silica	7.8	7.0	13.5	21.0	29.0	18.0	3.7
Marble	9.1	8.7	12.8	17.6	29.4	21.5	0.9
Trap rock	7.4	9.2	21.2	21.3	21.4	16.5	3.0
Argillaceous silica	6.0	11.0	21.0	22.0	21.5	17.5	1.0
Black slate	14.6	16.6	22.5	27.5	17.5	1.3	...
Tripoli	5.8	10.8	21.8	41.5	18.5	1.6	...

Preparation of Size-Graded Fractions

One hundred pounds of each powder were separated into five or six fractions by repeated passage through a laboratory size Federal air classifier. The particle diameters of the various fractions were as follows: <2, 2 to 5, 5 to 10, 10 to 20, and 20 to 40 microns. When possible a 40 to 75 micron portion was also obtained. During the transition from one fraction to the next larger, material was discarded in order to obtain a sharply defined range of particle size. Care was taken that at least 95 per cent of the material in each fraction was within the size limits assigned. The particle sizes were verified microscopically and many of the fractions were checked by determining the amount of under- and oversize by means of the laboratory air analyzer.

Methods for Determining Void Content

In order to calculate the void content of powders by any of the methods to be described, it was first necessary to determine the specific gravity of the mineral. All the powders were dried at 105° C. for several hours and cooled in a desiccator. A carefully weighed sample was then placed in a pycnometer, just covered with kerosene of known specific gravity, and the air removed from the powder by evacuation, the time necessary varying with the particle size and the nature of the powder. After filling with kerosene and adjusting to 25° C., the pycnometer was weighed. It was found that evacuation did not cause any change in the specific gravity of the kerosene used. Table II gives the specific gravities of the minerals in the various powders and fractions.

Table II. Specific Gravity of Minerals at 25° C.

Diameter Limits	Limestone	Silica	Marble	Trap Rock	Argillaceous Silica	Black Slate	Tripoli
Unfractionated powder	2.73	2.62	2.68	2.91	2.60	2.91	2.63
<2	2.74	2.60	2.56	2.81	2.50	2.88	2.62
2–5	2.74	2.64	2.67	2.82	2.50	2.84	2.64
5–10	2.73	2.65	2.64	2.86	2.53	2.85	2.63
10–20	2.72	2.66	2.69	2.90	2.58	2.92	2.63
20–40	2.72	2.64	2.65	2.93	2.64	2.93	2.62
40–75	2.69	2.64	2.73	2.94	2.62	..	..

It can be seen that in most cases the specific gravities of the finer fractions of a mineral are less than those of the larger, as has been found by Marshall (*10*) using very fine clays. This may be due to the incomplete removal of air from the fine fractions, although in the authors' work continued evacuation did not cause an increase in the specific gravities.

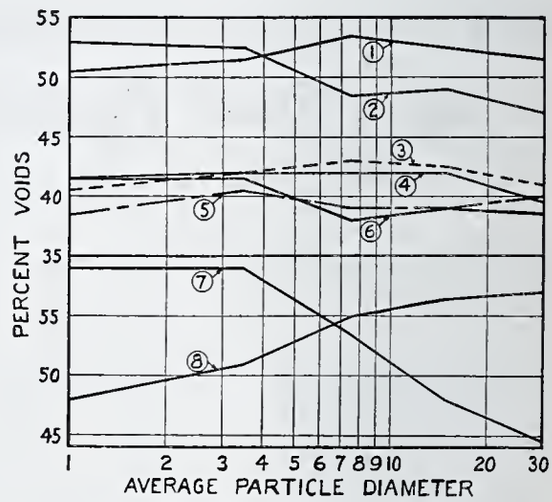

Figure 1. Void Content of Various Size Fractions by the Briquetting Method

1. Black slate
2. Soapstone
3. Silica
4. Marble
5. Limestone
6. Trap rock
7. Argillaceous silica
8. Tripoli

Three distinctly different methods which were fairly rapid and simple in operation were used to determine the void contents of the mineral powders. With proper care the results obtained by each procedure could be checked, although the three methods in most cases gave different results on the same powder.

Dry compaction is a method which is in common use to obtain the weight per unit volume of a compacted dust. In the authors' work cool, dry powder was compacted by hand tapping in a weighed, graduated glass cylinder. The weight and volume of the compacted powder were determined and the bulk density in grams per cubic centimeter (bulk specific gravity) calculated. From the values obtained the percentage of voids was calculated from the following equation:

$$\text{Per cent voids} = 100 - 100\,\frac{\text{bulk specific gravity}}{\text{specific gravity of mineral}} \qquad (1)$$

The void content of a powder can be calculated using its liquid absorption value, which may be obtained by several different procedures. Among them may be mentioned those of Barnard (*1*), Hougen and Hentzen (*5*), Klumpp (*6, 7*), Gardner and Coleman (*4*), and Bartell and Hershberger (*3*). The method used in this work was based on that of the last named authors. Assuming that the volume of liquid used was equal to the volume of voids in the compacted powder, the percentage of voids was calculated by substituting in the expression:

$$\text{Per cent voids} = 100 \frac{\text{volume of liquid}}{\text{volume of liquid} + \text{volume of mineral}} \quad (2)$$

A briquetting method based on that developed by Norton and Hodgdon (*11*) was also used. A 0.5 per cent solution of high-grade glue was added to the powder to give the same type of end point as in the liquid absorption method. The glue solution was necessary with the fractions containing particles larger than 10 microns in diameter to prevent crumbling of the dried briquets. That the adhesive had no appreciable effect on the void content of the finer fractions was shown by the fact that using water and the same technic, the results were almost identical. However, care must be taken that even a small excess of water or glue solution is not added to the powder. The carefully prepared wet mass was worked into place in a steel mold which was equipped with a removable bottom and a close-fitting steel piston or plunger. The piston was inserted and a pressure of 1.55 kg. per sq. cm. applied intermittently, by rocking the weight placed on the piston, thus causing vibration in the wet mass while it was being pressed. During this operation excess water was pressed out of the material and drained from the mold. As soon as drainage ceased, the wet compacted powder was removed and placed in a cool oven, the temperature of which was gradually raised to 105° C. When the briquet reached a constant weight, the dimensions were determined and the volume calculated. Knowing the weight and volume of the briquet the bulk density of the dry, compacted powder was computed. The percentage of voids was determined by means of Equation 1.

In order to determine whether or not higher pressures would effect greater compaction, experiments were made with pressures up to 46 kg. per sq. cm. With the apparatus used it was impossible at pressures above about 3 kg. per sq. cm. to subject the sample to vibration while under compression. Pressures above 1.55 kg. per sq. cm. did not cause a decrease in the void content values.

Comparison of Void Contents of Unfractionated Powders

The void contents of the unfractionated powders were determined by the three methods. The various liquid absorption values are not given, since they are all higher than those by the other two methods. Because of differences in particle shape, texture, and size distribution, the percentage of voids in the different powders varied widely. An inspection of Table III shows that the minimum void content was obtained for most of the powders by making a briquet under a pressure of 1.55 kg. per sq. cm. In the cases where the lowest value was not obtained by this procedure, it was attained by dry compaction. The percentage differences between the two methods in these cases were not large and probably approached the limits of experimental error. Soapstone, possibly because of the crushing of the soft particles which made up this material, was the only powder which gave a lower void content when briquetted under the higher pressure.

Table III. Percentage of Voids

	Briquetting 1.55 kg./sq. cm.	Dry Compaction	Minimum Value
	%	%	%
Limestone	31.5	30.0	30.0
Silica	32.7	36.6	32.7
Marble	33.0	37.4	33.0
Trap rock	33.0	40.0	33.0
Argillaceous silica	47.5	44.3	44.3
Soapstone	44.5	55.3	44.5
Black slate	47.2	57.0	47.2
Tripoli	54.0	52.6	52.6

Reference to the minimum values obtained shows that the materials fall into three groups. Limestone, silica, marble, and trap rock dusts with void contents between 30 and 33 per cent of the volume of the compacted powder make up the first group. Argillaceous silica, soapstone, and black slate dusts with void contents between 44 and 47 per cent comprise the second group. The higher void content of these powders is probably due to the greater irregularity in the shape of the particles and to other causes such as differences in texture and particle size distribution. Finally, tripoli has an unusually high void content, as would be expected for a dust composed of porous particles.

Comparison of Void Contents of Various Particle Size Fractions

Although the void content of each of the fractions of the various powders was determined by the three methods (water, kerosene, and Nujol being used in the liquid absorption method), to save space only the data for two representative powders are given in Table IV.

Table IV. Percentage of Voids

Powder	Fraction	Briquetting 1.55 kg./sq. cm.	Water Absorption	Kerosene Absorption	Nujol Absorption	Dry Compaction
Silica	<2	40.5	50.5	57.0	61.0	65.0
	2–5	42.0	48.5	54.0	59.5	58.5
	5–10	43.0	48.0	49.5	53.0	51.0
	10–20	42.5	45.0	44.0	47.5	42.5
	20–40	41.0	43.0	42.0	43.5	41.0
Black slate	<2	50.5	56.5	62.5	69.5	69.0
	2–5	51.5	55.5	60.0	65.5	66.0
	5–10	53.5	54.5	59.5	63.5	65.0
	10–20	52.5	55.0	56.0	59.0	59.0
	20–40	51.5	..	..	59.5	56.5

The dry compaction method does not give the void content of finer powders in a close-packed condition. Such packing of the finer fractions is not effected even by very gentle tapping. The presence of a film of adsorbed air acting as a cushion around each particle may be the cause of the high void content values obtained for the finer fractions by this method. It is also possible that the amplitude of vibration imparted to the small particles even by gently tapping is so great that the powder is maintained constantly in a loose-packed condition. With the coarser fractions the close-packed condition is more nearly approached.

The liquid absorption method usually gives a lower value for the void content with the finer fractions than does dry compaction. However, the value is dependent upon the liquid used for wetting, because that which has the greatest adhesion tension (*2*) for the mineral and the smallest film thickness on the particle will give the lowest percentage of voids. Of the three liquids used water was found to give the lower and kerosene and mineral oil (Nujol) the higher values. For the coarser fractions the method is occasionally unsatisfactory because the wet material does not form a ball.

Of the three methods used, briquetting is the most satisfactory for determining the void content of the finer mineral powders in a close-packed condition. Since the briquets do not shrink appreciably on drying, there is a possibility that the experimentally determined void content is greater than the true value by an amount equal to the small volume occupied, before drying, by the film surrounding the particles.

Figure 1 shows the minimum void content obtained by the briquetting method for all the fractions of the different powders up to and including the 20 to 40 micron fraction plotted against the arithmetic mean of the size limits of the fractions in microns. For fractions coarser than the 20 to 40 micron, the compaction method generally gives the lower value.

For tripoli the void content values for the finer fractions are less than those for the coarser. This is a porous material, and as it is crushed the capillaries are gradually destroyed;

thus with decreasing particle size the percentage of voids becomes smaller. The void content of the argillaceous silica decreases with increase of particle size. The finer fractions of this powder contain chiefly the softer clay; the coarser, the harder silica particles; and the intermediate fractions, mixtures of the two materials. The differences in void contents of the various fractions of this powder are probably due to the varying amounts of the two minerals composing them. The curves for marble, silica, limestone, and slate approach horizontal straight lines, indicating that for these materials particle size has no appreciable effect on void content. For trap rock and soapstone the curves indicate a higher void content for the finer fractions. The higher values are believed to be due to experimental difficulties encountered and not to increased void content associated with small particle size. With proper precautions the values obtained for the void content of the smaller fractions by the briquetting method show better agreement than those obtained by dry compaction or from liquid absorption data.

The void contents of the powders exclusive of tripoli and argillaceous silica decrease from slate to limestone. Since fractions of about the same size distribution are compared, the differences in void content of these powders may be attributed to differences in particle shape and texture. It was noticed on examining the powders under the microscope that, as the experimentally determined void content decreased, the particles became in general more regular and uniform in shape.

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A Modification of Bettendorff's Arsenic Test

With Adaptation for Mercury Determination

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The presence of mercuric chloride affects Bettendorff's test for arsenic. The addition of enough mercuric chloride to make its concentration 0.00001 M, before the addition of stannous chloride hastens the appearance of the coloration, increases the sensitivity of Bettendorff's test ten to one hundred fold, and enables the test to be made in a lower concentration of hydrochloric acid. Mercuric chloride in 0.00001 M solutions does not produce turbidity when stannous chloride is added. In the presence of mercuric chloride Bettendorff's test will detect a smaller quantity of arsenic than Gutzeit's test or Marsh's test. The rate of formation of the colloidal arsenic is a function of the concentration of mercuric chloride. Because of this, unknown concentrations of mercuric chloride as small as 0.00000002 M may be determined by comparing the rate of appearance of color in the unknown solutions with the rate of appearance in the presence of known concentrations of mercuric chloride.

When an excess of stannous chloride is added to a solution of a mercuric salt, a precipitate forms immediately. When an excess of stannous chloride is added to a solution of an arsenic compound in a high concentration of hydrochloric acid, a brown colloidal suspension of arsenic appears. If the concentration of arsenic is sufficiently great the suspension changes to a black precipitate. Frequently several minutes elapse between the addition of the stannous chloride and the appearance of the color due to arsenic. The delay in the appearance of the color is greater if the arsenic has been oxidized, as when arsenic sulfide is dissolved in hydrochloric acid and potassium chlorate. The greater delay persists even after the solution has been boiled to decompose the potassium chlorate. These facts seemed to indicate the possibility of testing for the presence of both mercuric compounds and arsenic compounds in the same solution by one addition of stannous chloride, if the precipitated mercury was filtered out immediately and the appearance of the coloration observed in the filtrate.

When an excess of stannous chloride was added to a solution containing compounds of both mercury and arsenic and the precipitate was removed as quickly as possible, no subsequent coloration of the filtrate appeared. It was evident that this procedure was useless as a simultaneous test for mercury and arsenic. However, very small amounts of a compound of mercury might hasten the appearance of the coloration due to arsenic in Bettendorff's test and be useful in shortening the time required for that test, or for increasing its sensitivity. The amount of mercury compound added to a solution to be tested for arsenic by Bettendorff's test must not be great enough to produce a turbidity due to the precipitated mercury.

Modification of Bettendorff's Test

The experimental work on the modification of Bettendorff's test consisted in determining the maximum concentration of mercuric chloride which will not produce turbidity when stannous chloride is added, and the effect of this concentra-

tion of mercuric chloride on the time of appearance of a coloration: (1) in cold solutions of varying concentrations of arsenic, (2) in solutions of arsenic in varying concentrations of acid, (3) in solutions of arsenic which had been boiled with potassium chlorate and hydrochloric acid, and (4) in solutions of arsenic which had been boiled with potassium chloride.

Reagents and Procedure

The solutions of mercuric chloride and arsenic trioxide were prepared by diluting 0.1 *M* stock solutions in volumetric apparatus. The C. P. arsenic trioxide, mercuric chloride, and hydrochloric acid as furnished by reputable manufacturers were used without purification for the making of stock solutions. For all series of experiments except the one in which the concentration of the acid was varied, all solutions were made in, and all dilutions were made by means of concentrated hydrochloric acid. A very nearly saturated solution of stannous chloride was prepared by dissolving 453 grams of $SnCl_2.2H_2O$ in 250 cc. of hot concentrated hydrochloric acid. After cooling, strips of metallic tin were added to prevent oxidation.

Each test was made with 10 cc. of solution prepared as follows: (1) the required amounts of mercuric chloride solution and arsenic trioxide solution were pipetted into a test tube, (2) concentrated hydrochloric acid to make a volume of 9.5 cc. was added, and finally (3) 0.5 cc. of stannous chloride solution was added and the contents of the tube were thoroughly mixed. The time at which the stannous chloride was added was noted.

Experimental Results

In the first set of experiments only mercuric chloride and stannous chloride were used. Table I shows the effect of 0.5 cc. of an approximately saturated solution of stannous chloride in 10.0 cc. of a solution of mercuric chloride varying in concentration from 0.001 *M* to 0.00001 *M*.

Table I. Effect of Adding Stannous Chloride

Molar Concn. of $HgCl_2$	Time Elapsing between Addition of Stannous Chloride and Appearance of: White cloudiness	Gray color	Opacity	Maximum darkening
	Sec.	*Sec.*	*Sec.*	*Min.*
0.001	10	15	20	1
0.0005	10	15	35	1
0.0001	15	1 min.	..	1
0.00005	20	..	..	20 sec.
0.00004	30	..	..	30 sec.
0.000025	1 min.	..	..	1
0.00002	2.5 min. (very faint)	..	..	2.5
0.00001	....	..	..	..

These data indicate that more than 0.00001 mole, or more than 2 mg. per liter, or more than 2 parts per million of mercury must be present to produce a visible turbidity when an excess of stannous chloride is added under the conditions of these experiments.

Table II presents a comparison of the times required for the appearance of the color in Bettendorff's test in the absence of mercuric chloride, and for the same test in the presence of 0.00001 *M* solutions of mercuric chloride, when the concentration of the arsenic trioxide was varied from 0.0005 *M* to 0.0000001 *M*. All tests reported in Table II were made at room temperature.

The presence of a trace of mercuric chloride so small that the mercury does not form a cloudiness visible to the unaided eye leads to a formation of an immediate brown coloration in a solution in which 10 minutes are required in the absence of the mercuric chloride. Besides, the sensitivity of the test is increased until only one-hundredth the concentration required for the uninduced test is required for the test when mercuric chloride is present. One ten-millionth mole of arsenic trioxide per liter represents 0.00015 mg. of arsenic in the 10 cc. observed in the test tube. Ten times this amount, 0.0015 mg. of arsenic, shows its presence in 20 seconds if mercuric chloride is present.

The sensitivity of the induced Bettendorff test equals or exceeds that of the Gutzeit (*2*) or Marsh test (*1*). No stain for comparative purposes in the Gutzeit tests is recommended by Blyth for less than 0.002 mg. of arsenic. No standard mirror for the Marsh test is shown by Blyth for any amount of arsenic between 0.001 mg. and no arsenic whatever. An investigation will be made in this laboratory to learn whether the determination can be made quantitative by a comparison of intensities of color.

Table II. Time Required for Appearance of Color in Cold Solution

(0.5 cc. of saturated $SnCl_2$ added)

Concn. of As_2O_3	Time Elapsing between Addition of $SnCl_2$ and Appearance of Brown Color in Cold Solutions: As_2O_3 in concd. HCl	As_2O_3 in concd. HCl and 0.00001 *M* $HgCl_2$
Mole/l.	*Min.*	*Min.*
0.0005	2.0	Immediately
0.0001	4.5	Immediately
0.00005	5.0	Immediately
0.00004	5.0	Immediately
0.00002	10.0	Immediately
0.00001[a]	10.0 (faint)	Immediately
0.000001	..	0.3
0.0000005	..	0.5
0.0000001	..	1.0

[a] In a review of the modifications of Bettendorff's test, Muhe (*7*) states that 0.0015 mg. of arsenic may be detected by the most favorable modification. In 10 cc. of a 0.00001 *M* solution of As_2O_3 there are 0.015 mg. of arsenic.

The ordinary scheme of qualitative analysis separates tin and antimony sulfides from arsenic sulfide by means of concentrated hydrochloric acid, and subsequently dissolves the arsenic sulfide in concentrated hydrochloric acid with the aid of potassium chlorate. There is some doubt whether arsenic pentachloride (*6*) forms, but whenever the arsenic is dissolved in this manner the excess chlorine must be driven out by boiling before the stannous chloride is added. After the boiling, the appearance of the brown color is delayed. Since the delay might be due to the presence of the potassium chloride formed, similar experiments in which an equivalent amount of potassium chloride was added were made.

Table III shows the results of these experiments. The times recorded are not comparable with those in Table II, for the experiments on which Table III is based were made on hot solutions while those on which Table II are based were made on cold solutions.

Table III. Time Required for Appearance of Brown Color in Hot Solution

(0.5 cc. of saturated $SnCl_2$ added)

Concn. of As_2O_3	Time Elapsing between Addition of $SnCl_2$ and Appearance of Brown Color in 10 cc. of Hot Solutions Containing: 0.1 gram $KClO_3$	0.06 gram KCl	0.1 gram $KClO_3$ and 0.00001 *M* $HgCl_2$
Mole/l.	*Sec.*	*Sec.*	*Sec.*
0.00001	120	60	40
0.00002	90	45	22

The data of Table III show that the presence of traces of mercuric chloride hastens the appearance of the brown color due to arsenic even after it has been boiled with an oxidizing agent, and that the presence of the oxidizing agent contributes to the delay, since potassium chlorate produces a greater delay than an equivalent amount of potassium chloride. This delay due to boiling with the oxidizing agent might be caused by: (1) the presence of free chlorine not removed by boiling, (2) the loss of arsenic chloride during boiling, (3) the loss of hydrogen chloride during boiling, or

Table IV. Concentration of Reagents and Time Required for Colloidal Arsenic Suspension to Become Denser than Standards *A* and *B*

Mercuric Chloride Concentration of standard		Final Concentration $\times 10^8$	Arsenic Trioxide 1×10^{-3} *M*	Hydrochloric Acid Concentrated	Stannous Chloride Saturated	Time Required			
						A		*B*	
	Cc.		*Cc.*	*Cc.*	*Cc.*	*Min.*	*Sec.*	*Min.*	*Sec.*
1×10^{-6}	45	90	2	0.5	2.5	2	22	4	40
1×10^{-6}	40	80	2	5.5	2.5	2	52	5	17
1×10^{-6}	35	70	2	10.5	2.5	3	19	6	10
1×10^{-6}	30	60	2	15.5	2.5	3	31	6	39
1×10^{-6}	25	50	2	20.5	2.5	3	54	7	31
1×10^{-6}	20	40	2	25.5	2.5	4	57	8	39
1×10^{-6}	15	30	2	30.5	2.5	6	6	9	58
1×10^{-6}	10	20	2	35.5	2.5	6	46	12	11
1×10^{-6}	9	18	2	36.5	2.5	7	25	13	12
1×10^{-6}	8	16	2	37.5	2.5	8	15	14	10
1×10^{-6}	7	14	2	38.5	2.5	8	51	14	56
1×10^{-6}	6	12	2	39.5	2.5	9	28	15	44
1×10^{-6}	5	10	2	40.5	2.5	10	9	16	40
1×10^{-6}	4	8	2	41.5	2.5	11	0	17	39
1×10^{-6}	3	6	2	42.5	2.5	12	7	20	2
1×10^{-6}	2	4	2	43.5	2.5	14	5	22	10
1×10^{-6}	1	2	2	44.5	2.5	17	0	27	10

(4) the presence of arsenic pentachloride. An attempt to determine which of these causes is effective is being made.

Bettendorff's test requires a high concentration of acid. It seemed possible that a lower concentration of acid might be effective in the presence of the mercuric chloride than in its absence. Tests showed that Bettendorff's test made in the absence of mercuric chloride would detect the arsenic in 10 cc. of 0.00045 *M* arsenic trioxide when the concentration of hydrochloric acid is 6 *M*, or in 10 cc. of 0.001 *M* arsenic trioxide when the concentration of the hydrochloric acid is 5.4 *M*. If the concentration of the arsenic trioxide is 0.001 *M* and that of mercuric chloride is 0.00001 *M*, a brown color is produced in concentrations of hydrochloric acid as low as 3.0 *M*.

Determination of Mercury

At the suggestion of H. H. Willard the authors attempted to determine mercury by observing the effect of the concentration of mercuric chloride on the time required for the reduction of the arsenic trioxide. This method for estimating the concentration of an inductor has been reported by Feigl and Krumholz (*4*), who determined bismuth by its inductive effect on the reduction of lead salts by sodium stannite; by Feigl (*3*), who determined silver by its inductive effect on the reduction of mercury salts by phenylhydrazine; and by Hahn (*5*), who determined silver by its inductive effect on the reduction of mercury salts by hypophosphites. Investigation showed that the concentration of mercuric chloride affected the rate of formation of colloidal arsenic in a Bettendorff test in which all other factors are kept constant.

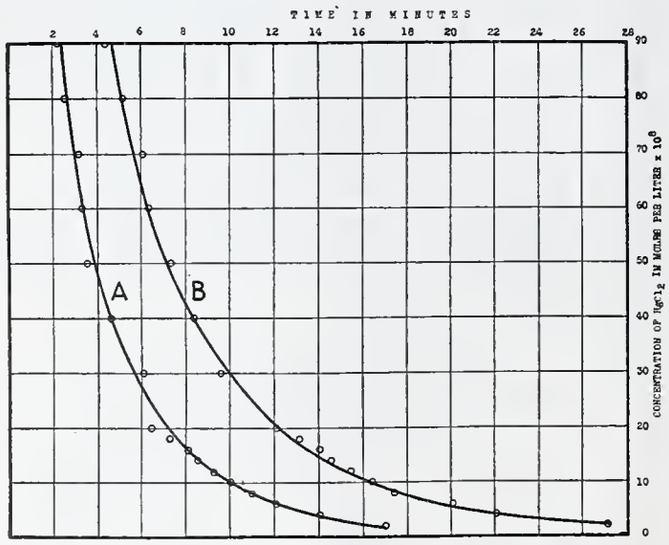

Figure 1. Determination of Mercury

At first, an attempt was made to determine the time required for complete reduction of 0.00002 *M* arsenic trioxide by a saturated solution of stannous chloride in the presence of varying concentrations of mercuric chloride. The time required for complete reduction increases as the concentration of mercuric chloride decreases, but the point at which reduction is complete could not be observed with as high accuracy as was desired. The time at which a changing suspension becomes definitely denser than an unchanging standard is more easily determined than the time at which reduction is complete.

Since the unchanging standard must be less dense than the completely reduced experimental sample, more than one standard may be used, and thus a reading on any experimental sample may be checked at any later stage of its reduction by comparison with a standard more dense than the first standard suspension.

The data reported in this section were secured by viewing from above 50 cc. each of suspensions contained in matched Nessler tubes standing in a rack above an inclined white porcelain slab exposed to light from the northern sky. Two comparison tubes, *A* and *B*, were employed. The procedure was as follows:

1. Standard solutions of all substances to be used and a supply of concentrated hydrochloric acid were provided.
2. The two comparison suspensions were prepared by adding 2.5 cc. of a saturated solution of stannous chloride to mixed solutions of such composition that when 2.5 cc. of a saturated solution of stannous chloride were added the resultant solution would be 50 cc. of solution 0.00001 *M* with respect to arsenic trioxide and 0.000002 *M* with respect to mercuric chloride for *A*, and 0.00002 *M* with respect to arsenic trioxide and 0.000002 *M* with respect to mercuric chloride for *B*. These solutions are completely reduced in a few minutes and the suspensions do not change in appearance for several hours.
3. The experimental tubes were prepared so that a 50-cc. sample of solution would be 0.00004 *M* with respect to arsenic trioxide (twice the concentration of the more concentrated standard) and from 0.0000009 *M* to 0.00000002 *M* with respect to mercuric chloride in different tubes, when 2.5 cc. of saturated stannous chloride were added.
4. Stannous chloride was measured into each of the experimental tubes from a buret and the time at which the addition was complete was noted for each tube. The contents of the tube were quickly mixed by stoppering and inverting.
5. Each experimental tube was placed in the rack near comparison tube *A* and the time when it became definitely darker than *A* was recorded.
6. The tube was then placed near comparison tube *B* and the time when it became definitely darker than *B* was recorded.

The data are recorded in Table IV and are represented by the curves in Figure 1. After the standard solutions were prepared, two persons (one preparing and comparing suspensions and the other recording data and making calculations) spent about 1.5 hours in collecting the data.

Since temperature, concentration of acid, concentration of arsenic trioxide, boiling with oxidizing agents, and the

concentration of stannous chloride if it is small are known to affect the rate of formation of the suspension, the time concentration curve should be determined by each analyst for the conditions under which he will make his determinations.

No substances were found to interfere with this determination except the noble metals such as gold and platinum which form colloids and obscure in whole or in part the colloidal arsenic.

Summary

1. When an excess of stannous chloride is added to mercuric chloride dissolved in concentrated hydrochloric acid, no cloudiness appears if the concentration of the mercuric chloride is as low as 0.00001 *M*.

2. Bettendorff's test made in the absence of mercuric chloride will detect the arsenic in 10 cc. of 0.00001 *M* arsenic trioxide dissolved in concentrated hydrochloric acid. The faint brown color appears in about 10 minutes.

3. When, in addition to saturated stannous chloride, enough mercuric chloride to produce a concentration of 0.00001 *M* is added to solutions of arsenic trioxide in concentrated hydrochloric acid, colorations appear immediately when concentrations of arsenic trioxide are as low as 0.00001 *M* and in one minute with concentrations as small as 0.0000001 *M* with respect to arsenic trioxide.

4. The presence of mercuric chloride hastens the appearance of the coloration due to arsenic in Bettendorff's test after boiling with potassium chlorate.

5. The presence of mercuric chloride reduces the concentration of hydrochloric acid required for Bettendorff's test from more than 5 *M* to 3 *M* when the concentration of arsenic trioxide is 0.001 *M*.

6. The time required for the appearance and development of the arsenic suspension is a function of the concentration of mercuric chloride in the solution. This behavior may be used to determine the concentrations of mercuric chloride in concentrations as low as 0.00000002 *M*.

7. The preferred procedure is to compare the increasing depth of color in experimental suspensions to prepared standards. Several comparisons may be made.

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Loading Combustion Tube in Carbon and Hydrogen Determination on Liquids

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In connection with research on petroleum bases, involving many analyses of liquid samples for carbon and hydrogen, the direct introduction of the sample into the combustion tube from a pipet has proved more satisfactory than the use of a boat or a glass bulb. A standard weighing pipet (Figure 1) of 2.5 cc. capacity is employed, and, to avoid trapping air at the delivery end of the pipet, a capillary hole *A* is drilled through the mantle below its ground-glass connection. In loading the combustion tube, a removable layer of copper oxide, constituting about half of the charge, is transferred to a Thiele reservoir of 100 cc. capacity, and then the tube is secured in a rigid vertical position in a stand (Figure 2) which carries a projecting plate at the lower end, with a cup *B* for insertion of the tube and a hinged clasp *C* above for keeping it plumb.

A brass pipet holder is attached to the combustion tube at *D;* the pipet, held at the stopcock with the index finger and thumb of one hand, is withdrawn from its mantle and the projecting end above the bulb is inserted through a circular hole (slightly inclined) in the guide plate *F*, far enough to allow the outlet end to pass into a slit leading to the conical seat *E*. On release of the pipet, the bulb is adjusted to its conical support and the pipet is centered automatically just above the combustion tube in such alignment that, on introduction of the sample, every drop descends to the permanent layer of copper oxide, without impinging along the sides of the combustion tube. The pipet can be quickly returned to the mantle for weighing and after the pipet holder is detached the Thiele reservoir is placed over the combustion tube and copper oxide shaken in above the sample.

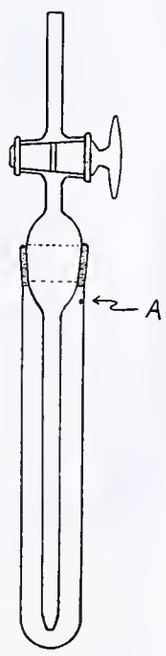

Figure 1

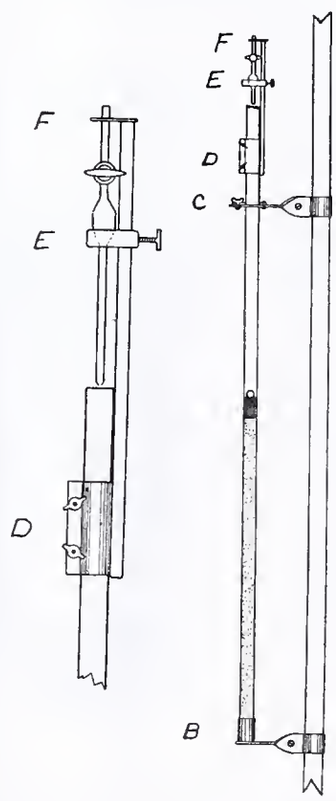

Figure 2

This procedure in analysis of liquids of low volatility insures complete combustion and reduces to a minimum the danger of a mishap in manipulation, which might result in loss or contamination of sample.

Acknowledgment

Credit is due W. L. Benson, mechanician in this laboratory, for construction of the metal equipment described in this paper.

Received February 17, 1933.

Apparatus and Methods for Precise Fractional-Distillation Analysis[1]

IV. Standardization of Low-Temperature Fractionation-Analysis Apparatus and Method Using Automatic Recording and Control

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The operation of the Podbielniak apparatus for low-temperature fractional-distillation analysis of gases and volatile liquids has been standardized by the use of an automatic recording and control mechanism, together with a further development and standardization of the fractionating unit itself. After the sample is in the column, the robot operator controls reflux cooling, regulates distillation rate according to the difficulty of fractionation, summons the human operator with a buzzer and trouble light whenever necessary, takes all temperature and pressure readings, and turns out a complete printed fractional-distillation curve, including a distillation time rate curve.

The robot is 80 to 90 per cent automatic, conducts distillations in less time, and is more dependable and accurate than the human operator. Through the use of this automatic recorder and control, the complete standardization of the low-temperature fractionation-analysis method resolves itself into the problem of deciding on sample sizes, distilling tubes, and a few adjustments of the operating mechanism.

THE present article describes an automatic recording and control mechanism in conjunction with an improved and standardized low-temperature fractional-distillation analysis apparatus, developed as the result of a comprehensive investigation (*3*) of all the fundamental variables or factors affecting the accuracy of the batch fractional-distillation method of analysis with the purpose of completing the development and standardizing the design of the apparatus and its parts, and adapting it to automatic operation, thus effecting substantial standardization of procedure. However, the automatic recording and control mechanism may be used with any low-temperature fractionating column designed for direct reflux cooling (No. 6, Figure 16, Nos. 8 and 9, Figure 17, Part II).

The fractionating unit shown in Figures 1 and 2 has been called the Standard Precision model because it has been designed specifically for highest practicable precision and standardization, whether manually or automatically operated.

Two Standard Precision low-temperature metal reflector-type (separate vacuum jacket and distilling tube construction) fractionating column assemblies are mounted on the right side of the apparatus in such a manner that either column may be used for analysis by simply turning stopcock *S*-2 and interchanging thermocouple and heater wires.

Both columns are of the same general construction and may be adapted for any kind of low-temperature analysis by simply inserting distilling tubes and flasks of proper specifications (*3*). The left-hand column is intended to be used for gas analysis, and is provided with a train of spiral caustic wash bottle and two drying tubes, one usually filled with calcium chloride and the other with either phosphorus pentoxide or dehydrite. This washing and drying arrangement is more efficient than that previously described and is essential with automatic operation to prevent traces of carbon dioxide or water vapor in the gas samples freezing and obstructing the column.

The provision of two columns on tap is convenient for alternate analysis of small gas samples and large gasoline or oil samples, inasmuch as a 2.6-mm. inside diameter tube may preferably be used for the former together with a 5-cc. distilling bulb, while a 4.0-mm. inside diameter tube with a 1000-cc. distilling flask may be used for the latter. Furthermore, mounting the two columns compactly on the same side is necessary in order to keep distillate flow lines as short as possible from the automatic control mechanism to either column.

The connections from the tops of the fractionating column distilling tubes to the upper stopcock manifold have been made 1 mm. bore with no excess dead space to introduce lag in the distillate measurements and excessive hold-up (*3*). For the same reason the glass tubing connections between stopcocks *S*-2 and *S*-3 have been made 2 mm. in bore, and the distillation pressure manometer tubing of approximately 3-mm. bore. While not shown in the diagram, a special distillation pressure manometer with a nipple connection at bottom and a mercury leveling bulb is provided for use with the micro 2.6- or 3-mm. distilling tubes, in order further to decrease dead space. To the left of stopcock *S*-3, the requirement for maintaining the dead space at a minimum becomes much less stringent and the connections are therefore made of much larger bores (3 to 4 mm.) to facilitate evacuation and flow of vaporous distillate. These apparently minor improvements are essential if the full accuracy of the automatic control mechanism and of the Standard Precision columns is to be utilized.

The distillate-receiving manometer is of the reëvacuable type—that is, the vacuum end is sealed with a special mercury-seal

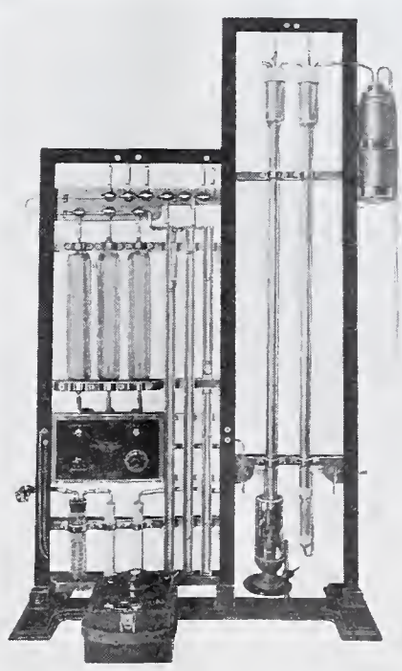


FIGURE 1. STANDARD PRECISION APPARATUS FOR LOW-TEMPERATURE FRACTIONAL-DISTILLATION ANALYSIS

[1] Book rights reserved except by permission of author.

The apparatus described in this paper are covered by foreign patents and pending United States and foreign patent applications and are manufactured and distributed exclusively by the inventor.

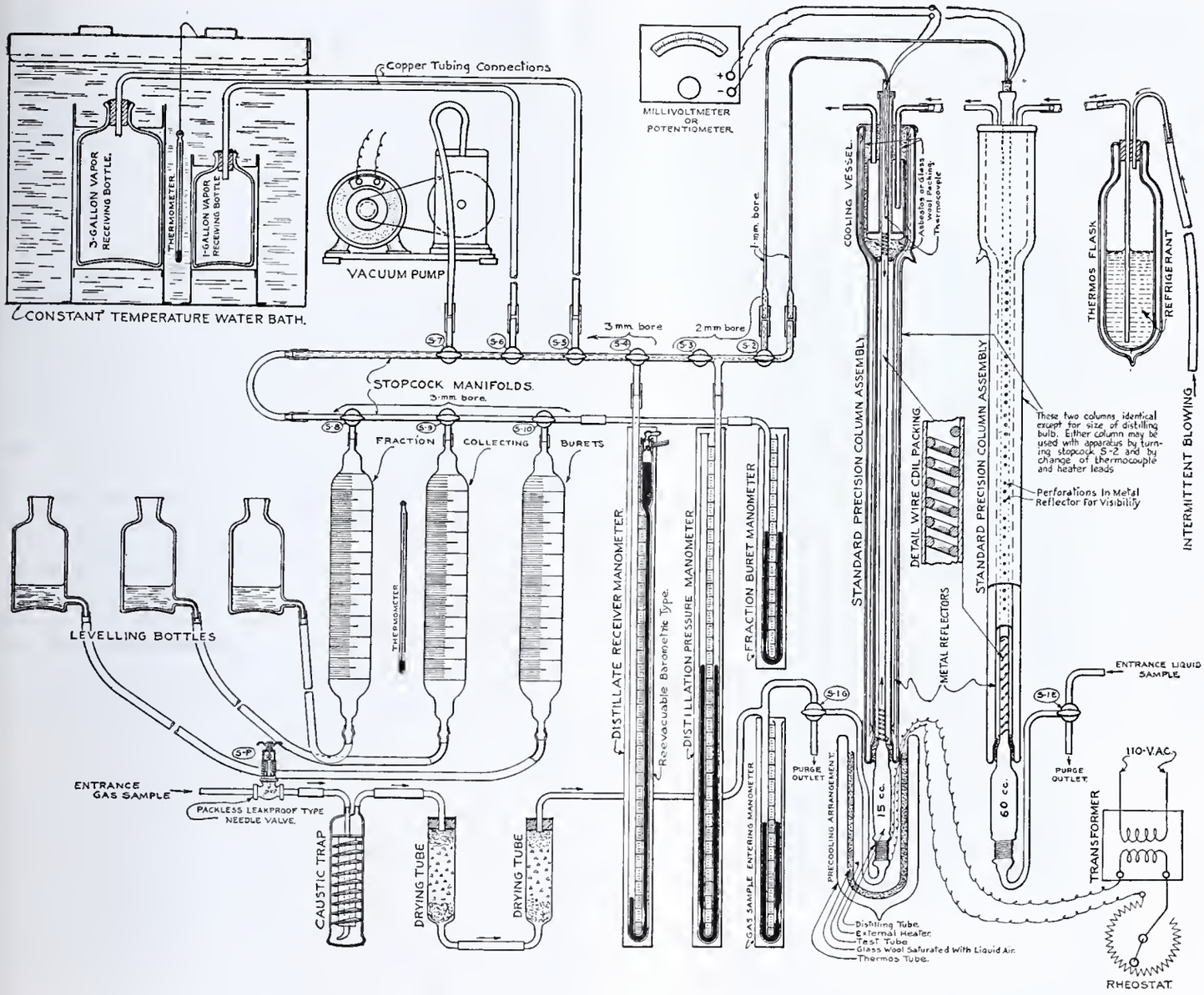


FIGURE 2. DIAGRAM OF STANDARD PRECISION APPARATUS

stopcock. Whenever the vacuum deteriorates sufficiently to affect the readings or when the mercury becomes dirty, it is a simple and convenient procedure to remove mercury, clean manometer, pour in clean mercury, and reëvacuate through the stopcock, using merely a suitable rotary oil pump such as the Cenco Hyvac. All this may be done without necessarily dismounting the manometer from the apparatus. It is not necessary to obtain a higher vacuum than about 0.01 mm. of mercury in the vacuum space. The long arm of the manometer is preferably calibrated and graduated by etching on the glass, to read directly in millimeters of mercury at 0° C. absolute pressure. For precise work correction should be made for effect of changing mercury level on vapor receiving system volume.

This type of manometer is convenient and accurate for manual operation. For automatic operation, it serves only as a check on the special compensated manometer incorporated in the automatic mechanism (Figure 4).

The fraction-collecting buret arrangement shown in Figure 2 is included in the Standard Precision model because of its convenience and accuracy in the analysis of highly complex samples by the procedure of breaking up the sample by fractional distillation into comparatively simple fractions containing very close-boiling components (or constant boiling point mixtures), and analyzing these fractions further by supplementary tests such as oxidation over copper oxide, absorption over reagents, etc. When the distillate is collected in these burets, the automatic apparatus applies only to control of reflux cooling and distillation pressure and to indicating reflux temperature.

The fractionating columns are of the Standard Precision metal reflector type (Figure 17, Part II, *3*). Standard specifications have been recommended both for the vacuum jacket and for a range of distilling tubes, including complete data on liquid and vapor hold-ups, maximum distilling capacities, and fractionating characteristics. For any definite analytical requirements of accuracy and sample size it is possible to select a distilling tube of proper specifications.

Automatic reflux cooling and control of distillation pressure positively require the use of the radiant dry packing type of cooling vessel and reflux chamber arrangement, shown in Figure 4, Part I (*2*), and further developed as described under Figure 17, Part II (*3*). Any type of gasoline or liquid reflux bath, such as used with the Regular, C. N. G. A., or spiral modifications (Figure 16, Part II) is inherently unsuitable for automatic operation because of the large time lag between entrance of refrigerant to the cooling vessel and the consequent cooling of reflux vapor and drop in distillation pressure. This difficulty may be overcome only by complicated devices, and therefore no provision has been made in the automatic mechanism for operation of other than Standard Precision or Precision fractionating columns.

The Standard Precision apparatus (Figures 1 and 2) is arranged for manual operation. To convert it to automatic

operation, it is only necessary to make certain connections as shown in Figure 4. For a complete description of the theory and details of manual operation of the distillation unit, the reader is referred to Part I (*2*).

A fairly large human element necessarily enters into the operation. The effect of the human element on the analysis results may be minimized by standardizing as much as possible on such details as sizes of samples to be taken, rates of distillation for various separations, exact method of changing distillation pressure, etc.; by standardizing the apparatus itself by careful training of the operator; by frequent checking of the operator's results against duplicates by same or other operator or against synthetic mixtures or against other methods of analysis. However, it will be obvious that the substantial elimination of the human element by the development and use of an automatic control and recorder is the logical solution to operational difficulties, either through direct use substantially to replace the human operator or through its tendency to lead to a better understanding of the principles of operation and to furnish an authoritative basis for comparison of fractionation unit modifications and adjustments and for standardization of manual operation.

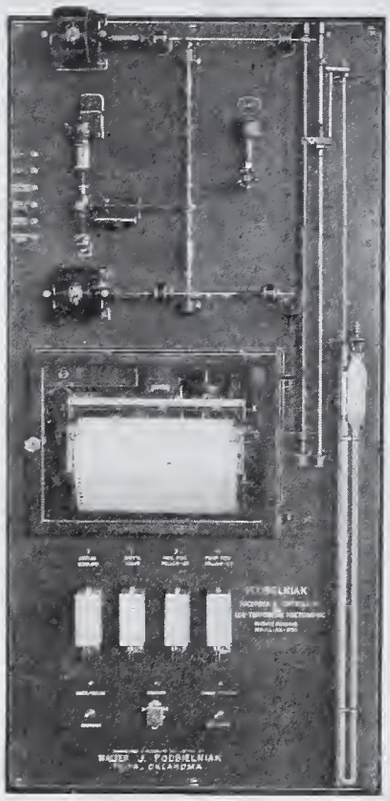


Figure 3. Automatic Recorder and Control for Operating Low-Temperature Fractional-Distillation Analysis Apparatus

Description of Apparatus and Operation

The general appearance of the automatic apparatus is shown in Figure 3. For aid in description, a diagram of the combined fractionation unit and recording and control mechanism, Figure 4, is presented.

Cooling of Reflux and Heating of Still. Liquid air must be admitted to the reflux chamber of the fractionating column in intermittent puffs in such manner as to maintain the column pressure as constant as possible at the desired value, as indicated on the distillation pressure manometer. Both the admission of liquid air and the heating of the still must be so conducted that the reflux liquid just wets the column packing wires without excess hold-up.

A fine iron or stainless-steel wire, insulated throughout except at its extreme lower end, is inserted into the open arm of the distillation pressure manometer so that its uninsulated extremity is a few millimeters above the point where mercury will rise at the desired distillation pressure. A return wire is sealed into the manometer near the bottom or inserted through a rubber tubing connection deep into the mercury of the right arm. As soon as the pressure increases sufficiently to cause the mercury of the manometer to make electrical contact with the point of the inserted wire, a circuit is completed through a low-voltage rectifier, through two wire contacts in the mercury, through the mercury, and through a sensitive telephone-type relay. The relay in turn operates a specially designed compact electromagnet valve which permits compressed air to blow liquid air into the reflux cooling vessel from a thermos bottle full of the refrigerant, as illustrated in the diagram. The exact regulation of compressed air admission to the thermos bottle is controlled by a small needle valve, and by a permanent fine leak, as illustrated. The introduction of liquid air into the reflux cooling vessel, using the direct cooling tubes, almost immediately lowers the pressure, whereupon the mercury in the distillation pressure manometer leaves the electrical contact, the relay circuit is broken, and the solenoid valve closes to cut off admission both of compressed air to the thermos bottle and of liquid air to the cooling vessel. Residual pressure in the thermos bottle is immediately dissipated by means of the leak already mentioned.

If the supply of liquid air should become exhausted, or the cooling vessel should plug up, or anything else should happen to interfere with the cooling, the column pressure will of course continue to rise in spite of the action of the automatic mechanism. Eventually the mercury will rise sufficiently to reach the bottom end of another wire to operate a second low-voltage circuit including a buzzer and a trouble signal light labeled "check reflux." The buzzer will summon the operator, while the light instructs him where to look for the cause of the trouble.

The supply of heat to the still may be controlled either manually or automatically. In manual operation, the operator will check the heat regulation whenever he happens to come to the apparatus and this will usually suffice. The requirement for heat increases normally, and if care be taken not to apply too much heat to the column at any time (as may be ascertained by watching the behavior of the liquid streaming down the column packing, for a minute or two) the worst that may happen from operator's prolonged inattention is a slowing up of effective distillation rate, without any detrimental effect to the accuracy of the results. Insufficient heat supply cannot cause a partial vacuum in the column, because of the functioning of another device described in the following paragraph.

For automatic regulation of heat supply a differential manometer connected to top and bottom, respectively, of the distilling tube, is used to actuate a relay which in turn shuts off heat supply to still whenever the pressure drop (proportional to flow of vapor through distilling tube) exceeds a predetermined amount. (This arrangement is not shown in diagram, Figure 4.)

Control of Distillation Pressure. The column pressure tends to remain constant, because of the action of the reflux cooling mechanism described in the preceding section. However, it rarely happens that the supply of heat at the still and the cooling of the reflux balance so nicely that there will not be sudden large drops in column pressure or continued partial vacuum. Such abnormal conditions, if per-

mitted, would of course destroy both the sharpness of fractionation and the accuracy of the reflux temperature readings. It has, therefore, been found necessary to insert still another contact wire in the distillation pressure manometer which functions like the other contacts already described, to actuate a relay, whenever the distillation pressure falls about 4 mm. below the distillation pressure. In this case the relay shuts an electromagnet valve in series with the distillate flow line from the fractionating column, thus completely stopping distillation, until the pressure again rises to break contact and to open the valve.

In this way column or distillation pressure is forced to stay between adjustable upper and lower limits. The exact adjustment of the various contacts involved is not critical, although certain definite positions for them have been worked out and found to result in smoothest action and greatest economy in the use of refrigerant. The two electromagnet valves for compressed air control and for distillate flow control, respectively, emit different sounds. As a result the operator can actually hear how well and how smoothly the regulatory mechanism is functioning and can immediately detect a wrong note, although he may be concentrating on some other task.

This distillation shut-off valve also acts as an accessory to the actual distillation-rate regulating valve described below. In other words, at breaks, where there is a tendency for column pressure to drop violently, the distillation shut-off valve shuts off the column for fairly long intervals at a time (because of slow comeback of pressure at breaks), thus giving the column a chance to fractionate out the last traces of the lower-boiling component remaining in the sample. Any operator of the low-temperature fractionating apparatus will appreciate that this valve duplicates human operation in this particular function, but more precisely and with 100 per cent dependability.

Recording and Plotting of Boiling Point and Quantity of Distillate. The fractional-distillation curve, which summarizes the results obtained by low-temperature fractionation is a plot of two series of observations: (1) reflux temperature and (2) pressure in the initially evacuated system receiving the distillate in vapor form. The ordinary temperature recorder, however, plots temperature against time. It was, therefore, necessary to develop means to operate the chart roller of the instrument in exact proportion to the pressure of the vapor-receiving system. A Bourdon-type gage with gear mechanism was not suitable because of its lack of precision and dependability. As will be appreciated by operators of the low-temperature fractionating apparatus, even the enlarged bulb-type barometric manometer used in the Standard Precision model must be read carefully, estimating to tenths of a millimeter, in order to develop the full accuracy of the apparatus.

The mechanism finally adopted as most accurate, dependable, and generally satisfactory consists of a combination of (1) a long slender contact rod with its lower extremity almost but not quite touching the mercury in one arm of a special manometer; (2) a special enlarged-bulb large-bore manometer with a gas-tight mercury-seal stuffing box on the arm in which the rod is inserted, and with the enlarged bulb and connection to vapor-receiving system on the other arm; (3) a carriage provided with a split nut to fit around a vertical threaded rod and with a clamp for the slender

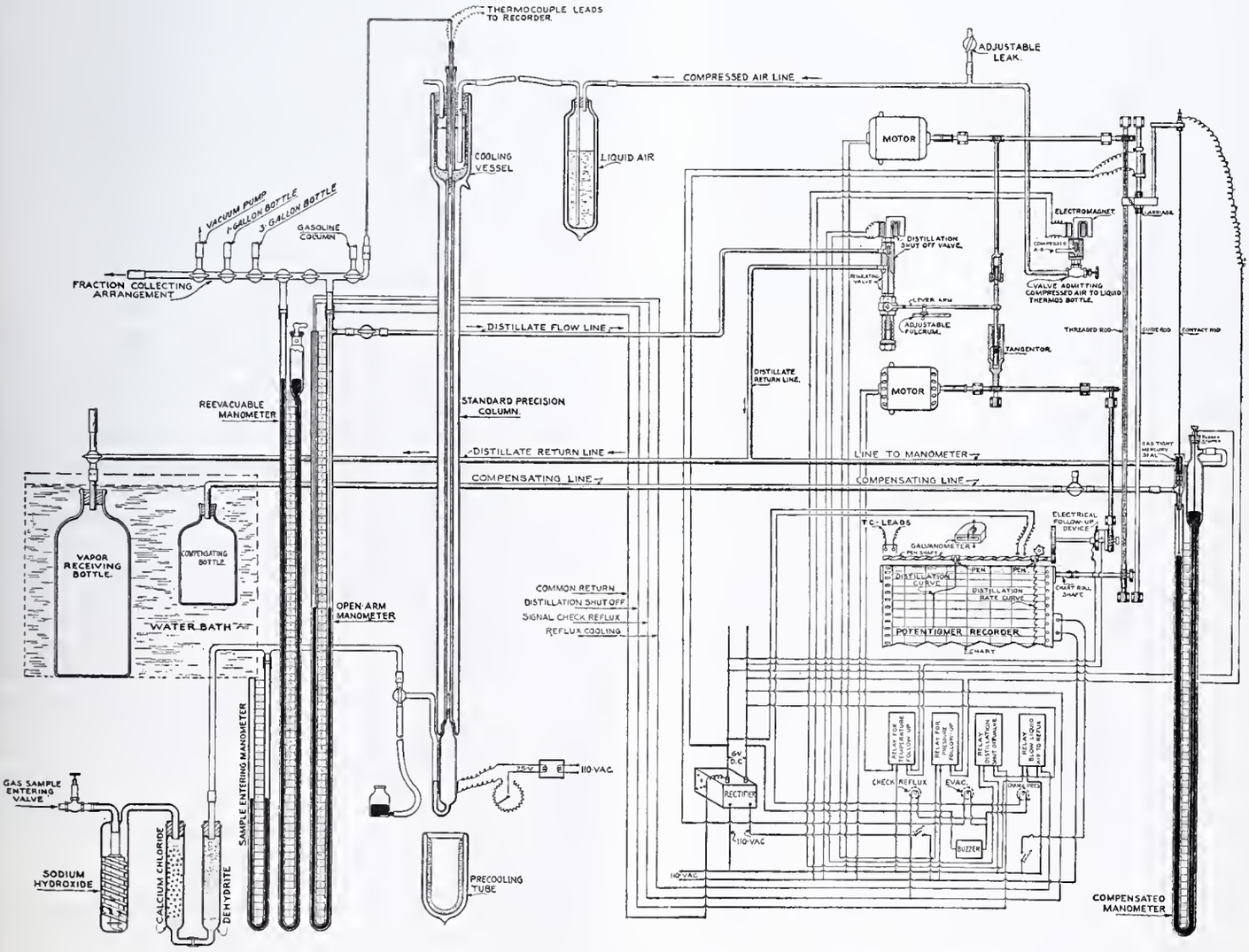


Figure 4. Diagram of Automatic Recorder and Control Apparatus

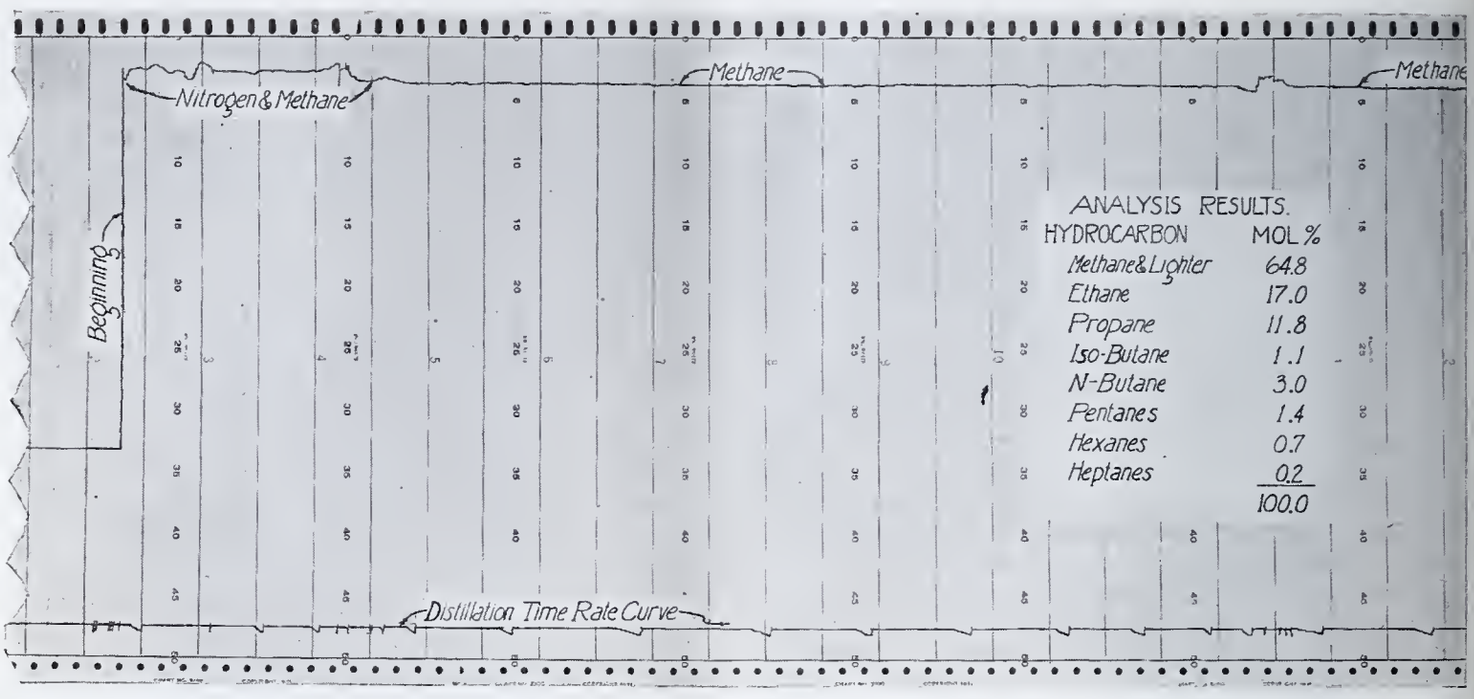


FIGURE 5. TYPICAL FRACTIONAL-DISTILLATION ANALYSIS CHART

contact rod already listed; (4) a low-voltage source and relay circuit completed whenever the contact rod touches the mercury; and (5) an electric motor actuated by the relay when the contact rod touches the mercury and which, through a train of suitable gears and the rotation of the vertical threaded rod in the carriage nut, simultaneously and in exact proportion raises the contact rod and rotates the temperature recorder chart until contact is broken between the contact rod and the mercury. By this action, the contact rod practically floats on the surface of the mercury with barely a 0.1-mm. gap, while the temperature recorder chart unrolls in proportion with the rise of mercury and thus plots the fractional distillation curve with much greater exactness than is possible by the method of manual readings of pressure and temperature.

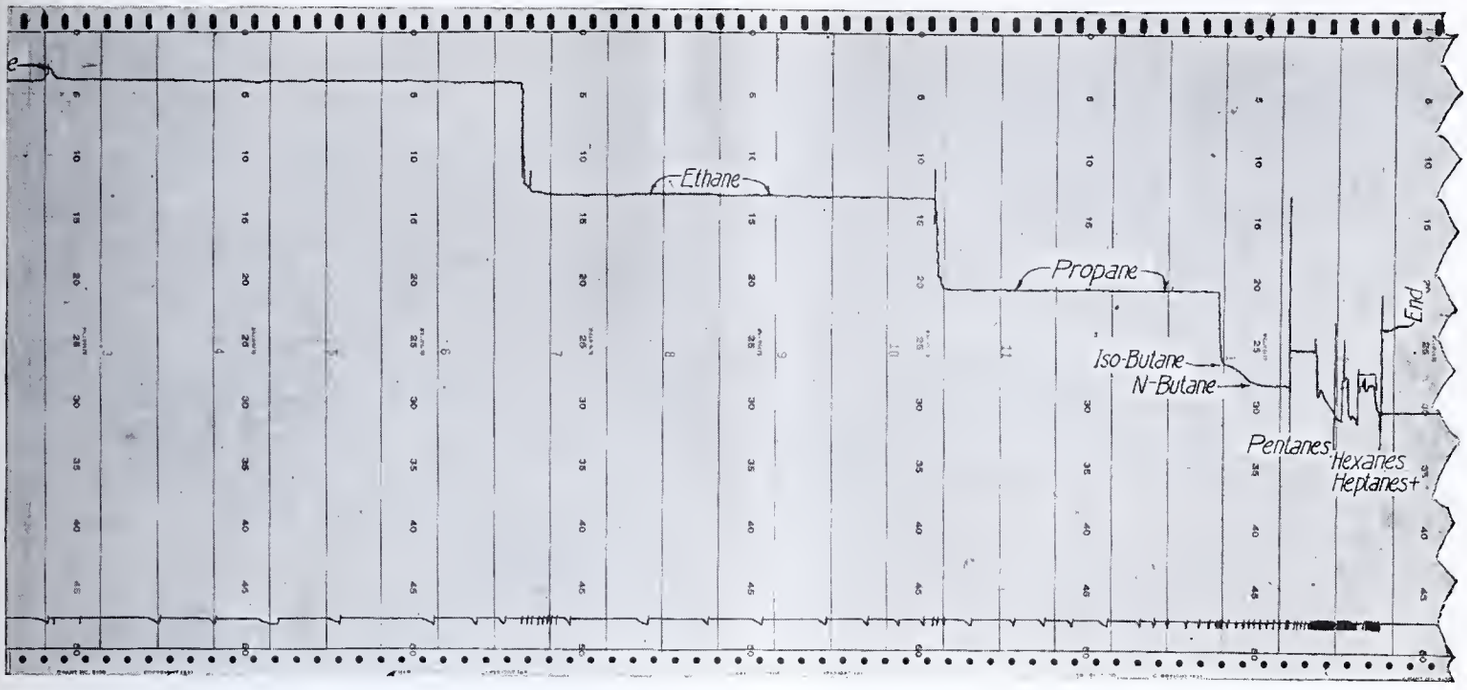
The question of compensation for variation of atmospheric pressure immediately suggests itself, since the manometer used is not of the barometric type. The solution to this problem was found by using a small mercury-seal packing box around the contact rod and by conducting a small tube from this arm of the manometer to a bottle of about 2 gal. (7570 cc.) capacity immersed in a constant-temperature water bath. This bottle is initially opened to the atmosphere before analysis is begun and then shut off. Nitrogen may be used in this part of the system to prevent oxidation of mercury. Since the mercury-seal stuffing box is absolutely gas-tight (*1*) for moderate pressure differences, the left arm of the manometer will remain at constant pressure even if the barometer varies 10 mm. or more during the analysis. The capacity of the compensating bottle is made about 2 gal. (7570 cc.), in order to minimize the change in pressure in the bottle due to change of mercury level in the manometer.

Finally, it is necessary carefully to calibrate the manometer for nonuniformity of bore and to prepare a chart for correction of the fractional distillation curve both for nonuniformity of bore and for the change in pressures of the vapor-receiving system and of the compensating bottle caused by the change of mercury level in the manometer. The correction chart is used only to correct distances between cut points on the finished distillation curve and its use entails little extra labor. It is possible to prepare correction charts for any combination of manometer and volumes of vapor-receiving bottle system and of compensating bottle, and results corrected with such charts are more accurate than is possible by manual readings and plotting. The chart is made to unroll in the ratio of approximately 1.8 (exact ratio determined by calibration) to the pressure rise in order to give a very open scale on the paper for accurate estimation of cut points (Figure 5). It should be noted that the abrupt drops in temperature in the butane plateau and beyond are due to lowering of distillation pressure in the usual manner. It has not been found necessary to introduce any device for automatically correcting temperatures for pressure, as the chart can be interpreted without such correction. Reevacuations are indicated on the chart by long inked lines perpendicular to the pressure axis and followed either by resumption of the plateau or by an abrupt shift of temperature due to change of pressure as just explained.

DISTILLATION RATE CONTROL. In the development of an automatic recording and control apparatus, considerable difficulty was experienced in solving the problem of regulating the distillation rate in approximately inverse proportion to the tendency of the temperature to rise. In other words, according to well-known fractional distillation theory and experience, the rate of distillation should be approximately inversely proportional to the instantaneous tangent of the fractional-distillation curve at any point. (In the case of this apparatus, distillation rate is inversely proportional to reflux ratio.) The manual operator solves the problem by changing the distillation rate in steps (*2*), and his greatest exercise of skill and judgment consists in the way he makes these changes to get the sharpest breaks in least total time for the distillation.

It was found necessary to develop both a special externally leakproof very small capacity regulating needle valve and an electrical contact follow-up device to take motion off the temperature-indicating parts of the recorder and to correlate this motion with the motion of the mechanism already described for unrolling the chart roll in such manner that the regulating valve would open (and close) inversely as the tangent of the fractional distillation curve.

In order to be able conveniently and in a practical manner to take motion off the temperature-indicating parts, the recorder must necessarily be of the potentiometer type rather than the millivoltmeter type. In the case of the Brown



Record Secured by Automatic Operation and Recording

potentiometer recorder, the spiral pen shaft indicated in the diagram revolves in exact accordance with the rise of temperature. Onto this shaft is therefore fastened an electrical contact follow-up device, very similar to the chart-rolling mechanism already described in that a relay-actuated motor simultaneously keeps the follow-up (more properly, run-away) contact piece out of electrical contact and also operates proportionately one end of a device called the "tangentor." The other end of the tangentor is actuated by the chart-rolling motor. The tangentor itself is simply a male-threaded member engaging a corresponding female-threaded member, both constructed so that the male member can travel only a limited distance either upward or downward before it slips out of threads and simply rotates until the relative direction of motion of the two parts is reversed, when the threaded parts again engage.

It will be noted that, essentially, the tangentor takes motion at one end corresponding to the rise of pressure in the vapor-receiving system; while at the other end it takes motion corresponding to the rise of temperature in the reflux. Depending upon the relative speed of rotation of the two motions, the male member of the tangentor moves up or down within its limits of travel, simultaneously opening or closing the regulating needle valve through the means of an arm and fulcrum arrangement. In other words, the opening of the valve is inversely proportional to the tangent of the distillation curve. A sharp rise in the fractional distillation curve, as it is being continuously and instantaneously plotted on the chart, almost immediately closes the valve. A small rise begins to close the valve. When the curve flattens out, the valve opens gradually. The regulation is truly proportional and may be made as sensitive as desired by the use of suitable gear ratios.

It is obvious that the distillation rate cannot be permitted to become zero at any point or the distillation would stop permanently at that point. Therefore, a micrometer adjustment is provided on the valve stem for the exact setting of a definite low rate to provide a minimal flow of distillate at breaks no matter how sharp. Also, there must be some means of regulating the maximum opening of the valve at plateaus; otherwise the capacity of the column might be exceeded. This requirement is met by a variable fulcrum on the arm connecting the tangentor and valve. These adjustments need be changed only when the distillation pressure is changed and to secure different degrees of accuracy or different total times of distillation.

The regulating valve must necessarily be made with great precision. The needle is of the actual dimensions of a medium-sized sewing needle with a seat of corresponding dimensions. In order to compensate completely for the disturbing force developed through difference in atmospheric pressure and in the pressure of the vapor receiving system, two flexible metallic bellows are incorporated in the valve construction as shown. The regulating valve is in series and immediately connected with the electromagnet shut-off valve.

In order to assist in the adjustment of the regulating valve and also to have a complete record of the functioning of the regulating means and of the entire automatic apparatus, an auxiliary pen on the recorder (towards the right of the chart) is made to jog every 75 seconds through a gear and cam mechanism operated by the recorder motor, as shown in Figure 4. This curve (Figure 5) shows the remarkably sensitive and more than human response of the regulating valve to every slight wiggle of the reflux temperature.

Certain noncontinuous functions, such as the actual entering of the sample, change of distillation pressure, reëvacuation of distillate receiver, use of fraction-collecting burets, etc., cannot be made completely automatic without undue complication of apparatus. Automatic signals are therefore incorporated in the apparatus so as completely to free the human operator from the necessity of attending the apparatus until the robot operator summons him by a loud buzz and then further indicates the reason for the summons.

The signals used are the following, as indicated over the corresponding trouble lights:

Reduce Distillation Pressure. When reflux temperature approaches room temperature, an electrical contact on the frame of the recorder operates to sound the buzzer and to light the red trouble light bearing the label as stated.

Reëvacuate. When the pressure in the vapor-receiving system reaches the maximum permissible for the hydrocarbon distilled, or when it approaches distillation pressure, an electrical contact device located on the smooth guide rod next to the threaded rod is actuated by the rise of the contact rod carriage to sound the warning buzzer and to light another red trouble light.

Check Reflux. This signal summons the operator when, for any reason, the cooling of the reflux becomes imperative.

Discussion

Figure 5 illustrates the results secured with automatic operation in the analysis of a natural gas. The presence of air or nitrogen is evidenced by the unduly low temperature and disturbances in the first portion of the methane plateau. The distillation rate or jog curve indicates the extremely sensitive and truly proportional regulation of distillation rate effected by the automatic control. As a result, the breaks of the curve are extremely sharp, considering that the curve is plotted on a pressure scale almost double the actual pressure rise. The chart itself is a standard 12-inch roll chart available for use with the Brown potentiometer recorder. (The recorder itself has been considerably modified.) Similarly, sharp curves may be secured for the distillation of natural gasoline, motor fuel, absorption oil, or other samples suitable for analysis in the low-temperature fractionating apparatus.

The automatic apparatus is inherently more positive and accurate than the human operator, as shown in Table I which gives a comparison of various analyses run in duplicate both by the robot and by a skilled human operator.

Table I. Typical Check Analyses with Automatic Control and Recording Apparatus

	Automatic Operation First run	Automatic Operation Second run	Manual Operation
Methane and lighter	64.99	64.95	65.1
Ethane	16.60	16.53	16.7
Propane	11.53	11.44	11.5
Isobutane	1.14	1.18	1.0
n-Butane	2.93	3.05	..
Pentanes	1.51 } 2.81	1.60 } 2.85	2.8
Hexanes and heavier	1.30	1.25	
	100.00	100.00	100.0

The saving of time on the part of the operator using automatic operation is very material. During its period of operation, the apparatus is from 80 to 90 per cent automatic, and the operator is free to do other work so long as he is within hailing distance of the automatic operator. The automatic apparatus plots the complete distillation curve in finished form and thereby saves the operator about an hour's time in plotting his readings and drawing the distillation curve. Automatic operation is inherently more efficient, so that the total time of distillation required to get results of any required accuracy is decreased considerably over that possible with even the most skilled human operation. For similar reasons the consumption of liquid air is reduced 15 to 20 per cent.

In spite of the number and complexity of the functions it performs, the automatic apparatus is neither a very complicated nor a delicate mechanism. The component parts (except the potentiometer recorder) are mostly gears, bearings, electric motors, telephone-type relays, etc., which in themselves are sturdy and not likely to cause trouble. The needle-regulating valve is not subject to action which would tend to damage it in any way. The electromagnet valves are of very simple construction. Leaks must of course not be present, as they would destroy the accuracy of the apparatus. However, the presence of leaks would be indicated on the plotted distillation curve. The practical usefulness of automatic operation would be considerably diminished if more trouble developed through it than naturally occurs with the distillation unit, but experience in the author's laboratory has shown that this possibility is not an actual one.

Influence on Standardization. The automatic recording and control apparatus represents a standardization of factor 3 (*3*) for low-temperature fractionations. The operator merely decides approximately what total time of distillation he desires and fixes a few adjustments on the controlling apparatus, with the assurance that the operation will give him a near approach to the best results possible for the particular fractionating unit and for the total distillation time used. The printed curve chart is unbiased, includes a check on the functioning of the distillation control in the form of a distillation time rate curve, and is in ideal form for inspection and criticism and for future reference. The curve is a complete record of the distillation and even reveals the possible poor functioning of the automat due to improper adjustments, leaks, or other troubles. Analyses run on the same sample in different laboratories by different operators but with the same apparatus and main adjustments should yield practically identical curves and results.

It remains to consider the standardization of decisions and functions not taken care of by the automatic apparatus which may be listed as follows:

1. Design of fractionating unit proper
2. Size of sample
3. Entering sample
4. Completing distillation
5. Automatic adjustments
   a. Contacts in distillation pressure manometer
   b. Distillation regulating valve adjustments
   c. Compressed air needle-valve adjustment
6. Choice of distilling tube and bulb on fractionating column of distillation unit
7. Manipulation of mercury seal and supply of heat to distilling bulb
8. General preparation and maintenance of distillation unit, involving evacuation, checking for leaks, cleaning, greasing stopcocks, etc.
9. General preparation and maintenance of automatic recording and control unit involving cleaning contacts, oiling and greasing when required, servicing, etc.
10. Miscellaneous

Fractionating unit design (1) has been discussed above. Any instrument, whether automatic or not, will require such preparation and care as are outlined in (8) and (9). The comparatively simple functions (3), (4), and (7) are readily standardized, and (2), (5), and (6) may be standardized by the preparation and use of a suitable standardization chart, taking into account the accuracy required, total time of distillation, etc. In this way substantially complete standardization of the low-temperature fractionating apparatus and its operation may be effected.

Acknowledgment

Grateful acknowledgment is made to the Brown Instrument Company for the use of a Brown potentiometer recorder during the period of experimentation and for whole-hearted coöperation on the adaptation of the instrument to this purpose.

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Wool Interests of Bradford, England, are carrying on extensive research work to develop a container for raw wool to replace jute sacks, according to the Commerce Department.

Wool manufacturers are said to object to certain features of the jute bag, among them the alleged tendency of jute particles to work loose and mix with the wool. The latest experiments concern a paper-yarn container. Bags made from this material have the appearance of canvas. The wood pulp is said to be available in unlimited quantities in Russia and the Scandinavian countries.

Microfractionating Column for Liquids Having Low Heat of Vaporization

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THIS small fractionating column was designed and made especially for the analysis of butenes according to the method of Dillon, Young, and Lucas (*2*), in which it is necessary to distill the butylene bromides under reduced pressure. Less than 10 ml. would be sufficient for an analysis if this amount could be distilled satisfactorily. Another microcolumn has been described by Cooper and Fasce (*1*), but this new column is somewhat easier to manipulate, especially with liquids having a low heat of vaporization, and gives about the same separation.

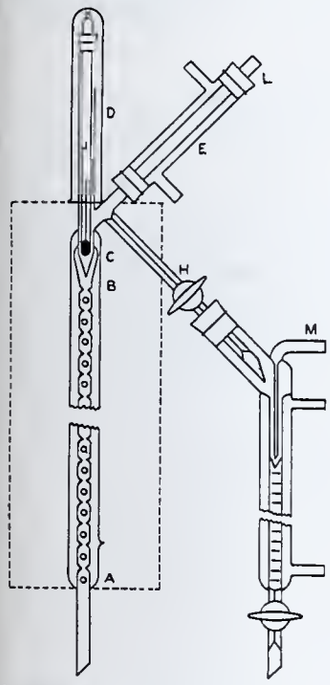

Figure 1. Microfractionating Column

Description

The new column is in general like the one of Cooper and Fasce, but it differs sharply in that total condensation occurs at the head of the column instead of partial condensation, and all the vapor must flow past the bulb of the thermometer instead of only the small fraction going into the receiver. This insures correct temperature readings with all substances, but some of the rectification is lost through elimination of partial condensation.

The column itself is of the Vigreaux type, 7 mm. inside diameter and 34 cm. long from *A* to *B* (Figure 1), made by heating small spots on the tube and indenting them with a wire. The upper end of the column is expanded into a bulb, *C*, into which is sealed a tube cut diagonally to a point to permit observation of the reflux. The uppermost tube, *D*, is about 3 mm. larger inside diameter than the Anschutz thermometer which it contains. The whole column is enclosed in an evacuated jacket around which is wound, on asbestos paper, a heating coil of No. 30 chromel wire. A test tube inverted over the thermometer protects it from drafts, while the column itself is packed in insulating material in the 10-cm. stove pipe indicated by dotted lines. All the vapor is condensed in the small water-jacketed condenser *E* and, as the liquid flows back over the entrance to the capillary stopcock *H*, some of it is withdrawn into the receiver, while the rest runs down the column. The receiver is a water-jacketed 5-mm. buret exactly as described by Cooper and Fasce.

Operation

The sample, about 10 to 15 ml., is placed in a 20-ml. flask, attached to the column, and heated by a microburner protected from drafts by a glass chimney (not shown). At first the stopcock *H* is closed so that all of the condensed liquid refluxes. The flame is adjusted to give a reflux of about 20 to 40 drops per minute at the point *C*, then the stopcock *H* is opened by tapping it gently with a pencil until distillate drops into the receiver at a rate of about 4 to 10 drops per minute. It is extremely important that a reflux ratio of at least 4 be maintained, or separation of the components will be very poor. For high-boiling liquids the chromel coil should be heated to about 20° below the observed boiling point. For distillation at reduced pressure, the pump is connected to both vent tubes, *L* and *M*. In plotting curves, allowance should be made for the small amount of liquid held in the capillary of the stopcock *H*.

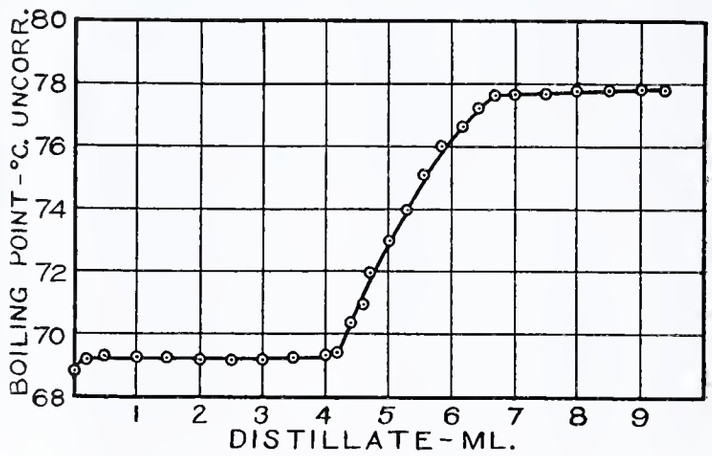

Figure 2. Distillation Curve of 1-Chlorobutane and 2-Chlorobutane

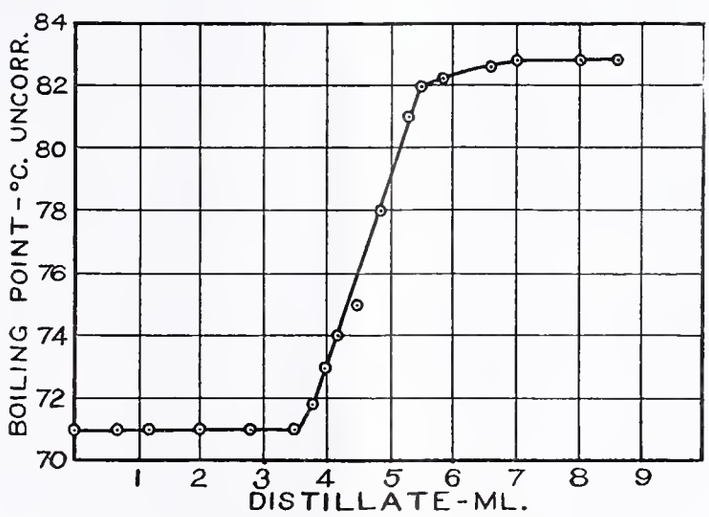

Figure 3. Distillation Curve of Aniline and Nitrobenzene

Typical Results

The two examples given below were chosen because they represent typical difficult cases. Obviously a mixture such

as methanol and water can be separated with ease. Figure 2 shows the boiling point curve obtained in the distillation of a mixture consisting of 5 ml. of 2-chlorobutane and 5 ml. of 1-chlorobutane. This mixture is very difficult to handle because the boiling points lie only 10° apart, and the heat of vaporization is low. Figure 3 shows the curve for a mixture of 5 ml. of aniline and 5 ml. of nitrobenzene at 10 mm. pressure. The hold-up in this case was greater because these substances are rather viscous.

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Received December 27, 1932.

A Rapid Volumetric Method for Determination of Sulfur in Coal and Coke[1]

Comparison of a Modified Benzidine Method with the Standard Methods

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A new modification of the benzidine sulfate method has been developed for the determination of sulfur in coals and cokes. Being a volumetric method, it is rapid and particularly suitable for routine determinations. It has the advantage that it can be used in conjunction with the usual calorific determination, eliminating the time-consuming barium sulfate precipitation. Results have been determined on fifteen coals and cokes of widely varying compositions, and comparisons have been made with sulfur values determined by the recognized standard methods. Comparison shows that it may be used as a substitute for these methods with a great saving of time.

Although the generally adopted methods for the determination of sulfur in coal and coke are entirely satisfactory from the standpoint of accuracy and ease of manipulation, they are somewhat time-consuming. The methods which have been adopted by the American Society for Testing Materials, the U. S. Bureau of Mines, and the American Gas Association, all depend upon the oxidation of the sulfur in the coal, and the subsequent precipitation as barium sulfate. It is well known that in order to obtain good results the solution containing the barium sulfate precipitate should be "allowed to stand for at least 2 hours or preferably overnight at a temperature just below boiling" (*25*). The present investigation was undertaken to develop a method for the determination of sulfur in coal and coke which would be satisfactory not only from the point of view of accuracy and of ease of manipulation, but also from the standpoint of the time element.

This investigation was directed toward the development of a suitable volumetric method, since this would be particularly advantageous for routine determinations. The methods involving the formation of sulfides by a thermit reaction with subsequent evolution of hydrogen sulfide and titration require a very precise and difficult technic to produce satisfactory results. Titration of sulfates with barium salts is subject to interference by appreciable amounts of calcium, nitrates, or ammonium chloride (*11*).

The authors' attention was called by V. K. Krieble to several published accounts on the determination of soluble sulfates by the use of benzidine. The method seems first to have been proposed by Müller (*19*) and was later modified by Raschig (*22*), von Knorre (*14*), and Friedheim and Nydegger (*7*). Subsequent applications of the benzidine method and modifications included the determination of sulfur in biologic liquids (*3, 6, 9, 13, 15, 20, 21*), rubber (*17*), organic compounds (*8, 16*), pyrites (*10, 27, 28, 29*), paper-mill liquors (*23*), oils (*4*), and coal (*12, 26*).

One of the faults of the benzidine method for general use is that appreciable amounts of the benzidine sulfate are always lost in the filtrate [for solubilities see Bisson and Christie (*2*) and Meldrum and Newlin (*18*)], even though saturated benzidine sulfate solution may have been used for washing the precipitate. It is obvious that the magnitude of the resulting error depends upon the volume of the original solution. It would be expected that for equal volumes of solutions the absolute error would be the same, but the percentage error would be much greater for smaller sulfate concentrations. This probably accounts for the fact that Heczko (*10*), for example, recommends the presence of not less than 0.3 gram of sulfuric acid for satisfactory results by the benzidine method. This source of error has been practically eliminated in the procedure described below, since the original solution containing sulfate ions is made up with a saturated solution of benzidine sulfate. This would not have been possible if the original oxidation of the coal had been carried out by the Eschka or sodium peroxide fusion method, in which case an additional error might have been caused by the presence of a high concentration of salts.

In order to give the method a thorough test, determinations were made on a large variety of coals and cokes varying not only in sulfur content but also in proximate analysis. Included in these were four coal samples which were supplied with complete analysis through the courtesy of H. M. Cooper of the U. S. Bureau of Mines.

For purposes of comparison, sulfur determinations were made by means of the standard bomb-washing and sodium peroxide methods (*1*), as well as by the new benzidine method. In the case of the Bureau of Mines samples, they were made by means of the Eschka method (*5*).

The results indicate that this new method can be used satisfactorily as a substitute for these standard methods.

[1] The preliminary experiments in this investigation were carried out by the senior author in 1920–21 at The Emerson Laboratories, Springfield, Mass.

Reagents

Saturated Benzidine Hydrochloride Solution. An excess of Eastman Kodak Company benzidine hydrochloride was mixed with water, approximately 8 grams per liter, and allowed to stand over a period of several days with occasional shaking. It was then filtered and stored in a dark bottle.

Saturated Benzidine Sulfate Solution. Benzidine sulfate was made by precipitation from saturated benzidine hydrochloride solution with a slight excess of sulfuric acid and was washed by decantation with large volumes of distilled water. An excess of this precipitate was mixed with water, shaken as in the preparation of the benzidine hydrochloride solution, and stored in a dark bottle. This solution was filtered into a wash bottle just before using.

Standardized Sodium Hydroxide Solution. It is advantageous to use a solution exactly 0.0624 *N* since 1 cc. is then equivalent to 0.1 per cent of sulfur when a 1-gram sample of coal has been used.

Phenolphthalein Indicator Solution. This solution was made by dissolving 0.5 gram of phenolphthalein in 100 cc. of 50 per cent alcohol.

Procedure

Weigh 1 gram of 60-mesh coal into the bomb calorimeter tray; use a smaller sample if the sulfur content is high. (An Emerson gold-lined bomb with a silica tray was used in this investigation.) Adjust the ignition wire (iron is satisfactory) and add a few cubic centimeters of water to the lower cup. Fill the bomb with oxygen to a pressure of 20 to 30 atmospheres, depending on the size of the bomb used. Take care not to add oxygen so rapidly as to disturb the sample. Set the bomb in cool water, and if no leaks are present, fire and let stand in water for not less than 5 minutes. Remove the bomb from the water and reduce to atmospheric pressure, taking not less than 1 minute. Wash carefully all parts of the interior of the bomb, including the tray, with a saturated water solution of benzidine sulfate, collecting the washings in a 250-cc. beaker.

The volume of the washings should be 100 to 150 cc. Add 60 cc. of saturated benzidine hydrochloride solution slowly and with constant stirring. (It has been the authors' experience that the slow addition of benzidine hydrochloride solution to the sulfate solution gives a precipitate which filters much more rapidly than if the precipitation is carried out by the reverse procedure. This corroborates the findings of Friedheim and Nydegger, *7*). The precipitate formed settles rapidly and can be filtered immediately on a small medium paper. Wash the precipitate with saturated benzidine sulfate solution until free from acid. Return the paper and precipitate to the original beaker, add 100 cc. of distilled water, and macerate the paper with a stirring rod. Titrate with 0.0624 *N* sodium hydroxide, using 1 cc. of phenolphthalein indicator solution. Just before the end point is reached, bring the solution to boiling and titrate to a faint pink. The number of cubic centimeters of alkali used divided by 10 gives directly the percentage of sulfur if exactly 1 gram of sample is taken.

Results

The results obtained on fifteen coals and cokes are tabulated in Table I.

It will be noted that the bomb-washing and benzidine methods were all run in duplicate and that the individual values obtained in each case checked satisfactorily by both methods, except for samples L and N in the case of the bomb-washing method and sample L in the case of the benzidine method, where the deviations were 0.14, 0.15, and 0.13 per cent, respectively. All the others checked to within less than 0.03 per cent, well within the permissible differences between individual determinations—viz., 0.05 and 0.1 per cent for coals containing under and over 2 per cent, respectively, and 0.03 per cent for coke (*1*). In the case of the Bureau of Mines samples, the benzidine method showed much less than the permissible differences in results as determined by two different laboratories—viz., 0.10 and 0.20 per cent for coals containing under and over 2 per cent in sulfur, respectively (*1*). From this point of view the benzidine method seems more desirable than the bomb-washing method, since only one deviation is noted in the benzidine method outside the permissible differences, and this, in a coal of abnormally high sulfur and ash contents.

The average values obtained by the benzidine method seem in general to be a few hundredths of a per cent higher than those by the bomb-washing method. The sodium peroxide results also run a few hundredths higher than those by the bomb-washing method, as was also noted by Selvig and Fieldner (*24*).

These results indicate that the benzidine method is entirely suitable for sulfur determinations in all types of coke or coal, for, as will be noted from the table, the cokes and coals employed varied tremendously in proximate analysis and sulfur content; the volatile matter varying from 2.05 per cent, sample C, to 36.40 per cent, sample M; the ash content, from 5.05 per cent, sample M, to 23.89 per cent, sample L; and the sulfur content from 0.39 per cent, sample E, to 10.75 per cent, sample L.

The chief advantage of the benzidine method over the other methods is that it requires much less time. It eliminates not only the time-consuming barium sulfate precipitation used in the other methods, but also the preliminary treatment of the sulfate solution which is required by the other methods. In fact, it will be noted that it is unnecessary even to filter off the ash remaining after the oxidation. As a result, a complete determination for sulfur can be run by this method in 30 to 40 minutes, as against 4 to 5 hours by the Eschka, and 2.5 to 3 hours by the bomb-washing or sodium peroxide methods. It is obvious that this method can also be used in conjunction with the determination of calorific value as in the case of the ordinary bomb-washing method. It is necessary only to wash the bomb with saturated benzidine sulfate solution and after making the customary titration to determine the acid correction, to proceed with the precipitation of the sulfate by benzidine hydrochloride. That the results by this procedure are quite satisfactory is indicated by the values for samples D and H which were so obtained.

Although the benzidine method as previously applied

Table I. Comparison of Sulfur Values on Various Types of Cokes and Coals as Determined by Different Methods

Sample	Fuel	Proximate Analysis: Moisture	Volatile Matter	Fixed Carbon	Ash	Sulfur Values by Various Methods: Sodium Peroxide	Bomb-washing: Individual	Bomb-washing: Average	Benzidine: Individual	Benzidine: Average	Eschka
		%	%	%	%	%	%	%	%	%	%
A	Coke	0.82	2.90	88.11	8.17	0.66	0.66, 0.64	0.65	0.66, 0.67	0.67	..
B	Coke	0.61	3.20	86.77	9.42	0.90	0.85, 0.87	0.86	0.89, 0.92	0.91	..
C	Coke	0.18	2.05	89.62	8.15	0.43	0.43, 0.41	0.42	0.44, 0.45	0.45	..
D	Anthracite coal	2.04	4.94	80.31	12.71	0.49	0.47, 0.48	0.48	0.48, 0.48	0.48	..
E	Anthracite coal	2.79	7.63	72.54	17.04	0.39	0.36, 0.38	0.37	0.39, 0.39	0.39	..
F	Semibituminous coal	1.44[a]	15.89[a]	71.90[a]	10.77[a]	..	3.59, 3.60	3.60	3.63, 3.65	3.64	3.60[a]
G	Semibituminous coal	1.57[a]	15.83[a]	76.35[a]	6.25[a]	..	0.87, 0.88	0.88	0.94, 0.94	0.94	0.94[a]
H	Semibituminous coal	1.12	16.75	73.37	8.76	0.76	0.73, 0.74	0.74	0.74, 0.75	0.75	..
I	Bituminous coal	1.01	23.36	69.02	6.61	2.09	1.90, 1.92	1.91	1.93, 1.94	1.94	..
J	Bituminous coal	0.91	24.75	63.00	11.34	1.32	1.28, 1.29	1.29	1.29, 1.29	1.29	..
K	Bituminous coal	2.03	26.73	66.11	5.13	1.44	1.35, 1.38	1.37	1.41, 1.44	1.43	..
L	Bituminous coal	1.10	24.46	50.55	23.89	10.72	10.58, 10.72	10.65	10.68, 10.81	10.75	..
M	Bituminous coal	1.26	36.40	57.29	5.05	0.90	0.81, 0.84	0.83	0.84, 0.85	0.85	..
N	Bituminous coal	1.85[a]	35.67[a]	51.50[a]	10.98[a]	..	3.73, 3.88	3.81	3.88, 3.89	3.89	3.81[a]
O	Bituminous coal	2.49[a]	34.98[a]	59.02[a]	3.51[a]	..	1.06, 1.08	1.07	1.10, 1.12	1.11	1.09[a]

[a] U. S. Bureau of Mines value.

seems to have required special technic (*17*, *22*), the authors believe that their modification has removed the objection raised by Mackay (*17*), that the "volumetric determination of sulfuric acid as benzidine sulfate proves troublesome unless great care and high analytical skill are employed, and is, therefore, unsuitable for use as a routine determination to be applied by an untrained staff."

Although the results above have been confined to coals and cokes, the authors have found that it is also applicable to fuel oils. In fact there is no reason to believe that it could not be used as a fairly general method for sulfur in organic compounds, judging from the fact that Garelli and Saladini (*8*) reported that an oxygen bomb can be used for the oxidation of organic compounds.

Since the method is both accurate and rapid and has proved particularly suitable as a routine method, it seems desirable for consideration as an alternate to the present standard methods.

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Estimation of Small Amounts of Antimony in Copper

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The separation of small amounts of antimony from large amounts of copper is a time-consuming operation. Several methods are in current use, probably the best known depending upon the tendency of a ferric hydroxide precipitate to occlude antimony. This method of separation is open to criticism, as has been noted by Blumenthal (*1*), who recommends the addition of potassium permanganate and manganese sulfate to the acid solution of copper. Manganese dioxide precipitates and carries down the antimony. Working with rather large amounts of antimony, about 50 mg. in 25 to 100 grams of copper, he succeeded in recovering it completely by means of a double precipitation with manganese dioxide. This procedure has been modified somewhat and combined with a spectrographic method for the purpose of estimating the extremely small quantities of antimony which are present in the best grades of refined copper. The results given in the tables were obtained by the following method:

Five hundred grams of copper were boiled with concentrated hydrochloric acid, washed with distilled water, and dissolved in concentrated nitric acid. The solution was boiled until free from fumes, diluted to about 2 liters, and ammonium hydroxide added until a slight permanent precipitate formed. This was dissolved with a little nitric acid and the solution again heated to boiling. Ten cubic centimeters of 3 per cent potassium permanganate solution were added and the boiling was continued for about 5 minutes. Fifteen cubic centimeters of a 5 per cent solution of manganous sulfate crystals were added and the boiling was continued for 10 or 20 minutes more, after which the beaker was allowed to stand undisturbed overnight.

The supernatant liquid was carefully decanted into a clean container and the precipitate brought onto an asbestos and glass wool filter, where it was washed free from copper nitrate with cold distilled water, using suction. The filtrate and washings were combined with the decanted portion, heated to boiling, and treated with permanganate, etc., as before. The precipitate was dissolved by pouring 50 cc. of concentrated hydrochloric acid over it, followed by a little water. The second precipitate was separated by putting the entire solution through the filter, and after washing was dissolved in the hydrochloric acid solution of the first. The solution of manganese dioxide and antimony was diluted to about 400 cc. and neutralized with ammonium hydroxide, after which 10 cc. of concentrated hydrochloric acid were added. Hydrogen sulfide was passed into the solution until precipitation ceased. The solution was allowed to stand undisturbed overnight and then filtered through glass wool and asbestos. The sulfides were washed with water and dissolved by pouring hot concentrated nitric acid over the filter, followed by hot concentrated hydrochloric acid and finally by distilled water. The filtrate was evaporated to 10 cc. in an open beaker on a hot plate.

One- or two-tenths cubic centimeter, accurately measured, of this concentrated solution was placed in a hole bored in the top of a pure graphite electrode. After drying at 100° C., the electrode was arcked for one minute, using a current of from 10 to 12 amperes at about 50 volts. The resulting spectrogram was compared with others prepared in the same way from antimony-free copper to which had been added known quantities of antimony. A comparison of the intensities of the antimony lines at 2598 and 2878 in the spectrograms of the known and unknown samples was made in the manner described by Nitchie (*2*). Another set of standards was prepared directly from pure copper chloride and accurately weighed antimony trioxide. The required amounts were dissolved, made up to 10 cc., and portions placed directly in graphite electrodes. The standards checked those prepared by the more lengthy process within the limits of error of the method, thus proving the completeness of the separation obtained in the process.

The sensitivity of the method may be increased by concentrating the antimony solution to a smaller volume, but this

necessitates a further separation of antimony from copper by means of sodium sulfide after the sulfide precipitate has been obtained. A few samples were treated in this manner, but no apparent increase in accuracy resulted. The presence of as little as 2 parts of antimony in 10,000,000 parts of copper can be shown by this procedure.

Table I. Antimony Determinations on Samples of Commercial Copper from Various Sources

Sample	Antimony
	%
1	< 0.00002
2	0.00006
3	0.00004
4	0.0002
5	0.0004
6	0.0004
7	0.001

Table II. Antimony in Unmelted Copper from the Lake Superior Mines

Nature of Sample	Source	Antimony
		%
Mass copper	Ahmeek mine	< 0.00002
Mass copper	Calumet and Hecla conglomerate	< 0.00002
Mass copper	Champion mine	< 0.00003
Mass copper	Isle Royale mine	< 0.00002
Mass copper	Osceola mine	< 0.00002
Mass copper	Quincy mine	< 0.00002
Copper oxide	Calumet and Hecla leaching plant	< 0.00002

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An Improved Head for Laboratory Fractionating Columns

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A STILLHEAD for ordinary laboratory distillations on a small scale is best made wholly of glass, fitted to the column (or to several columns of different lengths or types) by means of a ground-glass seat. The head should be strong, well balanced, and free from internal complications and also from readily broken external arms. If not in one piece, its parts should be connected by ground joints, rather than by rubber tubing, stoppers, etc. The head should be so designed as to provide variable reflux up to total reflux, to permit fairly accurate determination and control of the reflux ratio and accurate observation of the boiling point of the material being condensed, and also to deliver a cool distillate. Examination of a number of published designs (*1–7*, *9–12*) shows that these qualifications are not well combined in any one head.

Design of Head

It is believed that the design shown in Figure 1 satisfactorily incorporates the desirable features mentioned. The functions of the ground-glass seat *A*, the multiple ports *B*, and the drainage tube *C* are obvious. Partial condensation of vapors, yielding primary reflux, is effected by condenser *D*, which is cooled by water or air and is inserted through ground joint *d*. To obtain greater condensing surface condenser *D* may be made with a somewhat bulbous tip. The connecting arm *E* (which may be omitted) eliminates a possible dead vapor space about *D*. Condenser *G* is of double spiral type, and is seated in ground joint *H*. Condenser *I* reduces the temperature of the condensate. If high-boiling liquids are to be distilled, condensers *G* and *I* may be cooled by means of a current of air drawn through them, or by a stream of water passed very slowly, so that temperature differences between the hot vapor channels and the parts *G*, *H*, *I*, *J*, and *K* will not set up dangerous strains. The connecting tube *J* is of small bore (about 2 mm.), and is sloped as shown. During distillation part or all of the condensate from *G* and *I* may be returned to the column through this tube, thereby increasing the reflux, the distribution being determined by means of stopcock *K*. It is intended, however, that most of the reflux be produced by condenser *D*, thus relieving condenser *G* of heavy duty during ordinary distillations, while permitting operation at high or even total reflux. With high-boiling liquids it may be necessary to use condenser *D* little or not at all, as the incidental condensation in the head and the reflux through *J* may yield the desired reflux ratio. Tube *J*, because of its reduced bore, remains sealed with liquid even when all the condensate is drawn off as product. The slope of *J* should be slight, and the stopcock placed close to the junction, to minimize the volume of liquid held up at this point. The head is insulated, as indicated in the figure, by a covering of magnesia cement, applied as a paste made with water glass. The reflux ratio is ascertained by counting drops from *C* and from *L*. Drainage tube *C* is visible, as the column is glass-jacketed.

The short enclosed-scale thermometer *F* is seated in a ground joint, the inserted half of which is integral with the thermometer jacket. The thermometer is graduated from 20° to 300° in 1°; the length of the scale is 8.5 cm. Temperatures are observed through a short telescope lens (the type furnished with the Pregl microazotometer is satisfactory), and can be read to 0.1°. The thermometer is calibrated for immersion to the ground joint. The arrangements shown are considered preferable to the use of a thermometer-well long enough for total immersion of the mercury column, since such a space, when at the

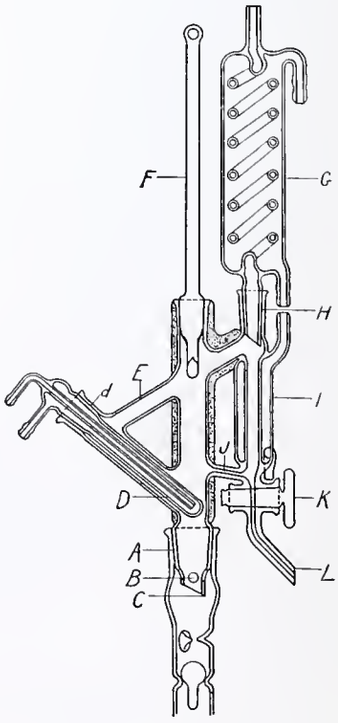

Figure 1. Diagram of Stillhead

Reduction is to one-fourth of actual size. Hose connections of condensers *G* and *I* are in the rear.

head of a column operated at moderate or low rate, cannot always be assumed to be filled with the vapors at the boiling point.

Advantages

This stillhead is entirely of Pyrex glass, with none but glass connections. It is compact, symmetrical, relatively small, and strong, with no easily broken projecting parts. With all condenser lines suspended the head is balanced and stable, requiring no support other than the ground-glass insertion at *A*. The head can be insulated completely without obscuring the internal drip-tube *C*, which shows the whole of the reflux. The thermometer is mounted vertically and is properly located. Two condensers are available for increasing the reflux, which may be varied up to total reflux.

The construction of this apparatus, while beyond the abilities of most amateurs, is not difficult for a good glass-blower. It is of course essential that the head be properly annealed immediately after making. Standard taper ground-glass joints (*8*) could probably be used at *A*, *d*, and *H*.

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A Method of Determining Solvent Properties of Volatile Thinners in Varnishes

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Various tests have been designed to determine the solvent properties of volatile thinners used in the manufacture of varnishes: titration with the thinner of a heavy-bodied linseed oil, a solution of kauri gum in butyl alcohol, or a solution of a distillation residue of kauri gum in turpentine, or gradual addition of the thinner to a short oil-kauri varnish of standardized composition as described by Holley (*1*), until precipitation occurs. These tests, however, can hardly be expected to give accurate information about the relative solvent powers of various thinners in varnish bases that may contain no kauri gum at all but instead various combinations of other resins of quite different solubilities (*2*). Moreover, it is to be expected that other ingredients of the varnish base, such as tung oil and linseed oil, will affect the solvent power of the thinner in the mixture, because the solvent power of a mixture usually differs widely from that calculated from its composition and the solvent powers of its components.

It seems preferable, therefore, in each case to measure the solvent power of prospective thinners by the amount of thinner that will cause incipient precipitation from the particular varnish base with which it is to be used. By this method the writer was able to select the proper thinner for a varnish in which precipitation formerly would take place on standing. Several difficulties, however, made an ordinary titration useless. The precipitation of gum, caused by adding too much thinner to the varnish base, took place very slowly, and the varnish was so dark in color that the precipitate could not be readily discerned; furthermore, the temperature of the solution had some effect upon the point of precipitation. As a result, the procedure was modified as follows:

Into each of five graduated test tubes were poured 5 to 10 ml. of varnish base, and the volume in each case was read off to 0.1 ml. To the five samples were then added 0.3, 0.6, 1.0, 1.5, and 2.0 volumes, respectively, of the thinner to be tested, and the samples were shaken thoroughly and left for one hour in a water bath maintained at 25° C. They were then examined for a precipitate, which, forming a lump at the bottom of the tube, or adhering to the glass, was easily recognized by slowly turning the tube upside down. To increase the accuracy, a new series of determinations was made between the last tube without a precipitate and the first tube with a precipitate—for example, between the tubes containing 0.6 and 1.0 volumes of thinner, respectively. With most thinners the minimum volume causing precipitation, designated as solvent power, could easily be determined with an accuracy of 10 per cent.

Table I. Solvent Power of Petroleum Distillates

Sample	Distillation Range	Solvent Power
	° C.	
1	37–217	0.7
2	38–222	0.6
3	94–174	0.8
4	99–175	0.7
5	149–188	1.0
6	144–206	0.7
7	146–222	0.8
8	147–229	0.8
9	150–228	0.8
10	183–249	0.9
11	184–254	1.6
12	38– 66	0.5
13	66– 79	0.5
14	79– 93	0.4
15	93–107	0.6
16	107–121	0.6
17	121–135	0.6
18	135–149	0.7
19	149–163	0.7
20	163–177	0.7
21	177–191	0.7
22	Residue	0.9
23	99–107	0.6
24	107–121	0.7
25	121–135	0.7
26	135–149	0.7
27	149–163	0.8
28	Residue	0.8

Some results of this test applied to various petroleum distillates are given in Table I. Samples 1 to 11 are refined commercial petroleum fractions. Samples 12 to 22 were obtained by Engler distillation of sample 2, and samples 23

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to 28 by a similar distillation of sample 4. In general, the solvent power of petroleum fractions toward the particular varnish base used in this investigation increases with decreasing volatility. This is definitely shown by samples 12 to 28, in spite of the small irregularity exhibited by sample 14. However, the volatility is not the only factor of influence, as shown by the first 11 samples. Sample 5 is a better solvent than sample 6 of nearly the same volatility, sample 11 is far better than sample 10, and sample 3 is as good a solvent as sample 9 which has a considerably lower volatility. Such variations point to the test as a valuable guide in the selection of the best thinner.

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A Microtest for Triaryl Carbinols

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A COMMON indication of the presence of triaryl carbinols is the appearance of a color upon solution in sulfuric acid (*3*, *4*). This reaction falls short of being specific since there are a number of other substances such as benzophenone (*6*), dibenzalacetone (*6*), fuchsone (*5*), and triphenylmethyl peroxide (*2*), which likewise give a color in sulfuric acid. In the synthesis of certain triaryl carbinols the authors were faced with the problem of detecting traces of the desired product in the presence of a considerable amount of ketone or ester. They therefore developed an accurate test which depends on the conversion of the carbinol into the chloride and then into the free radical. The reaction was carried out in a capillary tube on a microscale in which the color of the free radical was observed readily. Moreover, as the air diffused slowly into the tube the color was discharged gradually and the insoluble peroxide was precipitated. This provided a very sensitive check on the observation of color. The method was found applicable to a number of triaryl carbinols.

Procedure

Reagents. Precipitated silver was made by the addition of zinc dust to a solution of silver nitrate. The precipitate was washed with 1 per cent sulfuric acid, with water until neutral, and then with alcohol, ether, and anhydrous ether. Since the powder still contained adsorbed water, it was covered with benzene and the latter distilled until after the distillate was no longer cloudy. It was then washed with anhydrous ether and stored in a desiccator over phosphorus pentoxide. A commercial grade, Mallinckrodt's silver metal precipitated, was tried later in the work and found to be entirely satisfactory.

Eastman acetyl chloride was used in the tests.

Micro Test. Capillary tubes, similar to melting point tubes except that they were about 1 to 2 mm. in diameter, were first made. One of these tubes was used as a reagent vessel according to the general method described by Fuchs (*1*). Approximately 1 mg. of the tertiary aryl carbinol was put into one of these tubes and covered with acetyl chloride. The material was stirred with a micro stirring rod made by drawing out an ordinary glass rod to a size small enough for the micro reagent vessel. After a short time the acetyl chloride was evaporated by inserting a micro tube and blowing a current of dry air over the mixture. The crystals so obtained were washed with a small amount of dry petroleum ether, using approximately the same volume as was used of acetyl chloride. The petroleum ether was admitted through a micropipet made by drawing out the tip of a dropping funnel. After stirring the crystals in the washing liquid, the tube was put into a small centrifuge to throw the chloride to the bottom. The washing liquid was then removed by means of the micropipet and a small quantity of silver powder added. Enough dry benzene to fill the tube approximately one-sixth to one-quarter full was admitted and the mixture stirred with the micro stirring rod or a fine silver-plated wire. Upon centrifuging, the silver powder was thrown to the bottom of the tube. The liquid layer remained colored from the presence of the free radical. The color could be seen better by holding the tube against a sheet of white paper or toward diffused daylight. Even when the color was only a faint yellow it was observed easily. As oxygen diffused slowly into the narrow tube the liquid became decolorized, owing to the formation of the peroxide. This effect traveled slowly downward through the tube and formed a very striking confirmation of the presence of the free radical from the carbinol.

Semi-Micro Test. The reaction was also carried out with 10 mg. of material in a 4-mm. outside-diameter tube. This semi-micro test was more convenient in many respects because it did not involve the use of such fragile reagent vessels, pipets, and stirring rods.

Considerable latitude was found to be possible in the quantities of acetyl chloride, silver, and solvents used. The test was applied successfully to mixtures of triphenylcarbinol with ketones and esters, and to 1 mg. of pure triphenylcarbinol. Smaller amounts were not tried. Other carbinols and halides which gave positive results were dixenylphenylcarbinol, trixenylcarbinol, α-naphthylphenylxenylcarbinol, α-naphthylphenyltolylcarbinol, and α-bromo-*p*-benzhydryltetraphenylmethane. Negative tests were obtained with triphenylmethyl peroxide, benzophenone, and triphenylmethane. An extremely faint test was given by triphenylmethylethyl ether.

Zinc dust was used in place of silver for some tests, but the latter was more active. Mercury gave erratic results, probably because of poor contact.

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Determination of Nuclear Halogens in Organic Compounds

A Critical Study and Standardization of the Stepanow Method

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The Stepanow procedure for the determination of nuclear halogen has been subjected to a critical study because of the controversial opinions regarding its accuracy. Through a study and change of certain factors influencing the precision of the results, a standardization of the procedure has been effected. The application of this method to the analysis of halogenated nitro compounds is described in detail for the first time.

DURING a study of the halogenation of *m*-diphenylbenzene, one of the problems under investigation in this laboratory, it became necessary to analyze a number of hitherto unreported compounds for halogen. Early in this work, it was found that the Carius method was unsatisfactory, because of consistent and incomplete decomposition of the sample. The well-known sodium peroxide fusion method of Lemp and Broderson (*5*) also proved unsatisfactory. Other investigators (*4*) experienced similar difficulties in the application of each of the above-mentioned methods in the analysis of the chlorinated biphenyls. The authors then considered the possible application of the Stepanow method (*8*) as modified by Drogin and Rosanoff (*2*) for halogen analyses, and again the results obtained were quite unsatisfactory. However, in view of the many possible advantages of the Stepanow method (*8*) over the peroxide fusion and the Carius methods, it was decided to subject the former method to a thorough and critical study with the object of developing a procedure which would be of general application for the determination of nuclear linked halogen in organic compounds.

The original Stepanow procedure (*8*) has been made the subject of investigations by Bacon (*1*), Walker and McRae (*10*), Maryott (*6*), and Drogin and Rosanoff (*2*), and, more recently, by Proner (*7*), Van Duin (*9*), and Favrel and Bucher (*3*). Favrel and Bucher proposed a substitution of isoamyl alcohol in place of ethyl alcohol in the original Stepanow method. They contend that successful application of the latter method in the case of nuclear substituted halogen depends not only on the proportion of sodium employed, but also on the temperature of the reaction mixture during the reduction, and that the higher the temperature, the more nearly the experimental values approach the theoretical halogen content. Their procedure is similar in general to methods previously cited with the exception that the reaction mixture, after reduction is complete, is diluted with water and extracted with additional portions in a separatory funnel. The combined water extract after acidification with nitric acid is treated with an excess of silver nitrate and the quantity of the latter equivalent to the halogen determined either by a gravimetric precipitation of excess silver nitrate as silver chloride or by a Volhard titration of excess silver with standard thiocyanate. These investigators admit that their method cannot be used for volatile substances, even though a reflux condenser was employed during the reduction, and they also state that attempts to substitute an alcohol of even higher boiling point than isoamyl alcohol—benzyl alcohol—yielded unsatisfactory results, the nascent hydrogen being consumed largely in the reduction of the alcohol itself.

PROCEDURE

The procedure employed and described herein is a modification of that by Drogin and Rosanoff (*2*):

A sample of the organic compound with a halogen content equivalent to 30 to 35 cc. of 0.1 *N* silver nitrate is weighed into a small glass vial and transferred to a dry 500-cc. Kjeldahl flask fitted with a Liebig reflux condenser with the constricted tip of the latter previously removed. The quantities of ordinary absolute alcohol and metallic sodium (Merck blue label grade) to be added were calculated from the empirical equations given by Drogin and Rosanoff. In several cases it was found necessary to increase the quantities of alcohol and sodium required, and reference to these particular instances are made elsewhere in this article. The alcohol is then introduced into the flask and heat applied cautiously to dissolve the sample (if possible). The weighed quantity of sodium, from which the oxide had been previously removed, was cut in rodlike lengths of 2.5 cm., kept under kerosene, and thoroughly dried with filter paper before introducing into the alcohol mixture, through the top of the condenser. The reaction mixture is occasionally shaken and approximately 0.5 hour is sufficient to complete the addition of the sodium. The reaction mixture is heated gently for at least one hour after the last portion of the sodium has been added (in exceptional cases heating for a longer period of time is necessary). A darkening of the reaction mixture at this point is of no importance. The flask and contents are then cooled until lukewarm and carefully diluted with 200 cc. of water, adding the first portion cautiously so as to avoid a violent reaction due to traces of unreacted sodium. A strip of litmus paper is added to the diluted reaction mixture and, if the halogen is chlorine or bromine, the solution is carefully acidified with 6 *N* nitric acid, adding the latter in 10-cc. portions with shaking and occasional cooling of the reaction mixture with tap water. If the halogen is iodine, the flask and its contents are cooled in a mixture of crushed ice and water and a normal solution of nitric acid, previously chilled, added in small portions until the solution is just faintly acid to the litmus paper. In no case should more than 10 cc. of excess nitric acid reagent be present at the end of the neutralization. Furthermore, the solution should be kept cold until the solution of standard silver nitrate bas been added. If the litmus paper turns blue after an iodide solution has been acidified, the results are likely to be low due to oxidation of hydriodic acid and consequent loss of halogen. The contents of the flask are then transferred quantitatively to a 600- to 800-cc. beaker and approximately 8 to 10 cc. excess over the calculated quantity of 0.1 *N* silver nitrate solution added dropwise from a buret with continuous stirring of the mixture during the addition. To facilitate rapid filtration of the solution, the silver halide precipitate is allowed to stand for 5 minutes to complete coagulation and settling of the insoluble material and then filtered into an 8-cm. funnel fitted preferably with a grade of filter paper especially prepared for filtration of agar in the preparation of culture media. (Filter paper 5250, Arthur H. Thomas Company catalog.)

Regardless of whether the compound analyzed contained chlorine, bromine, or iodine, it was found necessary to filter off the precipitated silver halide which was quite discolored after coagulation and settling. The precipitate is thoroughly washed with distilled water and the filtrate and washings are collected in a liter beaker and then transferred to a large porcelain evaporating dish (2-liter capacity) and 10 to 12 cc. of saturated ferric alum–nitric acid indicator solution added. In a few analyses, particularly those of nitro derivatives, the solution gives evidence of a slight darkening after the indicator solution is added. With the further addition of 10 to 20 cc. of 6 *N* nitric acid, the solution becomes much clearer and lighter in color. A 0.1 *N* ammonium thiocyanate solution is added slowly with stirring. In the immediate vicinity of the end point the thiocyanate solution is added in portions of 2 to 3 drops until the end-point color is definitely observed.

Contrary to the observations of Drogin and Rosanoff (*2*), a blank correction must be established for the titration, even though the reagents employed in the procedure are found to be halogen-free. This blank correction has been found to be independent of the quantities of alcohol and metallic sodium employed in the analysis. As will be noted also, the blank value is a personal factor and is dependent upon the color intensity of the end point to which the individual titrates. Therefore, it is necessary that the determination of the blank value and the volume ratio in which the silver nitrate and ammonium thiocyanate solutions react, the standardization of the solution, and the analysis proper, all be carried out under identical conditions with respect to final volume of solution titrated, acidity of solution, quantity of indicator employed, and titration in the large porcelain dish.

The results of the analysis of a variety of halogen-substituted aromatic derivatives as obtained by following the above described procedure appear in Table I.

Table I. Halogen Content of Compounds Analyzed[a]

	Compound Analyzed	Halogen Theoretical	Halogen Found
		%	%
1.	Chlorobenzene	31.52	31.28
2.	*o*-Dichlorobenzene	48.26	48.39
3.	*p*-Dichlorobenzene	48.26	48.39
4.	1,2,4,5-Tetrachlorobenzene	65.71	65.69
5.	Chloranil	57.65	57.63
6.	Hexachlorobenzene	74.74	74.71
7.	Benzene hexachloride	73.16	72.77
8.	Bromobenzene	50.92	51.11
9.	*p*-Dibromobenzene	67.77	68.11
10.	Tetrabromophenolphthalein	50.44	50.45
11.	9,10-Dibromoanthracene	47.58	47.32
12.	2,5-Dichloroaniline	43.78	43.83
13.	*p*-Bromoaniline	46.47	46.30
14.	*p*-Bromoacetanilide	37.34	37.31
15.	Iodoform	96.70	96.49
16.	Iodobenzene	62.22	62.01
17.	*p*-Iodoacetanilide	48.63	48.89
18.	*B*-Iodonaphthalene	49.97	49.86
19.	*p*-Chlorotoluene	28.03	27.90
20.	6-Chloro-3-aminotoluene	25.06	24.89
21.	5-Bromo-2-aminotoluene	42.96	43.06
22.	6-Bromo-3-aminotoluene	42.96	43.19
23.	4-Bromo-3-aminotoluene	42.96	42.61
24.	4-Bromo-3-benzoylaminotoluene	27.55	27.84
25.	4-Bromo-3-acetaminotoluene	35.06	35.43
26.	3-Bromo-4-acetaminotoluene	35.06	35.04
27.	*m*-Nitrochlorobenzene	22.52	22.45
28.	*p*-Nitrobromobenzene	39.57	39.93
29.	*p*-Nitroiodobenzene	50.98	51.03
30.	4-Nitro-2-chlorotoluene	20.67	20.77
31.	*p*-Chlorobenzoic acid	22.66	22.68
32.	*o*-Iodobenzoic acid	51.18	50.93
33.	*p*-Chlorobiphenyl	18.81	18.75
34.	3-Methyl-6-chlorobiphenyl	17.51	17.61
35.	3-Methyl-4-bromobiphenyl	32.35	32.27
36.	3-Methyl-6-bromobiphenyl	32.35	32.45
37.	4-Chloro-1,3-diphenylbenzene	13.40	13.62
38.	4-Bromo-1,3-diphenylbenzene	25.88	25.98
39.	3-Phenyl-4-chlorobenzoic acid	15.25	15.18
40.	Methyl ester of 3-phenyl-4-chlorobenzoic acid	14.38	14.47
41.	Benzyl ester of 3-phenyl-4-chlorobenzoic acid	10.99	11.13
42.	3-Phenyl-4-bromobenzoic acid	28.85	28.81

[a] Duplicate analyses checked within 0.1%, in nearly all instances.

In the original Stepanow procedure (*8*) no need of a blank correction existed, because of purity of the reagents, removal of solvent after reduction with sodium, and carrying out of the titration in a limited volume of approximately 150 cc. Other methods deviated in various ways from the original Stepanow procedure and therefore a blank correction is necessary. Drogin and Rosanoff (*2*) pointed out that a blank correction was required because of the presence of traces of halogen in the metallic sodium employed, and therefore their value was dependent on the weight of sodium. However, because of a limitation of the sample weight to 0.2 to 0.3 gram, their blank value did not undergo any appreciable variation. The authors found that the blank correction is independent of the quantity of sodium and alcohol used, and furthermore it represents a correction for the sensitivity of the end point in the volume of the solution as titrated.

Determination of Blank Value

In order to determine the value of the blank correction, varying quantities of sodium from 0 to 14 grams, inclusive, are dissolved in proportionate quantities of absolute alcohol (as calculated from the equations proposed by Drogin and Rosanoff, *2*), refluxed one hour, cooled, and then diluted. The diluted solution after acidification with 6 *N* nitric acid is then treated with a measured volume (20 to 30 cc.) of standard silver solution, filtered, and the filtrate titrated with standard ammonium thiocyanate (ferric alum as indicator). The blank value (cubic centimeters of silver nitrate) represents the difference between the volume of silver nitrate originally added and the volume of silver nitrate equivalent to the thiocyanate required in the titration. For the authors' solutions, this correction was 0.1 cc. (an average of ten blank determinations, with the maximum deviation of any single value not exceeding 0.03 cc. from the average value). In the actual calculations of an analysis, this blank value was added to the volume of excess silver nitrate solution as determined from the back titration with ammonium thiocyanate and the resulting sum subtracted from the volume of standard silver solution originally added. The difference is equivalent to the halogen in the sample taken.

It should be pointed out that very little reference is made to the analysis of halogenated nitro aromatic compounds. Stepanow (*8*) reports the analysis of one such compound and Favrel and Bucher (*3*), another. The authors have analyzed four such compounds and the results are given in Table I. It was found that the quantities of sodium and alcohol proposed by Drogin and Rosanoff (*2*) were insufficient for complete reduction of such compounds. Illustration of this point is given in Table II.

Table II. Effect of Increased Quantities of Sodium and Alcohol on the Analysis of 2-Chloro-4-nitrotoluene

Run	Sodium and Alcohol Excess	Halogen Theoretical	Halogen Found
	%	%	%
1	None	20.67	17.75
2	20	...	18.07
3	50	...	19.65
4	100	...	20.43
5	150	...	20.77

The data in column 2 of Table II refer to the excess over the quantities of sodium and alcohol proposed by Drogin and Rosanoff (*2*). In each of the first four analyses, evidence for incomplete reduction of the sample appeared in the form of a reddish azo or azoxy precipitate, the quantity of the latter diminishing with increasing quantities of sodium and alcohol taken. No such red precipitate was detected in the final analysis of this series. Therefore, it should be noted that in the analysis of the nitro compounds reported in Table I not less than 150 per cent excess of the quantities of sodium and alcohol proposed by Drogin and Rosanoff (*2*) were employed. These observations are in accord with the proposed mechanism of the reduction of aromatic compounds as suggested by Favrel and Bucher (*3*). They state that reduction of the benzene nucleus to a cyclohexane derivative occurs before cleavage of the carbon-halogen linkage. Consequently, an excess of reducing agent would be necessary for halogenated aromatic nitro compounds, both to reduce the nitro group and to produce the halogenated cyclohexane derivative from which the halogen is readily removed.

Inasmuch as Drogin and Rosanoff (*2*) also proposed the introduction of not more than a 3 to 4 cc. excess of the standard silver nitrate solution in the precipitation of halide in the sample, it was considered advisable to study the effect of the addition of an increasingly larger excess of silver solution on the accuracy of the method, with the hope that no appreciable adsorption or occlusion of precipitant would occur, and that consequently the end-point sensitivity of the indicator would be increased. The results obtained in this phase of the study appear in Table III.

Table III. Effect of Increased Excess of Precipitant upon Precision of Results

Compound Analyzed	Excess of $AgNO_3$ Added (Over theoretical)	Halogen Theoretical	Halogen Found
	Cc.	%	%
1. *p*-Chlorobenzoic acid	4	22.66	22.78
	8		22.60
	12		22.68
2. *p*-Bromoacetanilide	4	37.34	37.45
	8		37.31
	12		37.31
3. Bromobenzene	4	50.92	51.17
	8		51.15
	12		51.11
4. 1,2,4,5-Tetrachlorobenzene	4	65.71	65.58
	8		65.59
	12		65.69
5. Iodobenzene	4	62.22	61.79
	8		61.91
	12		62.01

It is apparent that the larger excess of standard silver nitrate accounts for smaller differences between the theoretical and experimental halogen percentages. But the primary reason for the use of a larger excess of the standard solution is that the end-point transition seemed much sharper than ordinary, because of the increased quantity of silver thiocyanate appearing in the back-titration.

Summary

In the determination of nuclear halogen in organic compounds, by the method described, the effects of a variation of several factors were studied and the following conclusions attained:

1. Drogin and Rosanoff (*2*) limit the sample weight to 0.2 to 0.3 gram, regardless of halogen content of the material analyzed. Consequently a high percentage error occurs in the analyses of substances of low halogen content. The authors have found it advisable to adjust the sample weight in accordance with the halogen content, so that it is equivalent to 30 to 35 cc. of 0.1 *N* $AgNO_3$.

2. The blank determination, the volume ratio of silver nitrate to ammonium thiocyanate and the standardization of the silver nitrate (against C. P. sodium chloride) must be carried out under parallel conditions of acidity, volume of solution titrated, and titration in the large porcelain dish.

3. The analysis of halogenated nitro compounds requires an excess over the quantities of sodium and alcohol specified by Drogin and Rosanoff.

4. The method is not suited to the analysis of volatile substances. Preliminary attempts to determine the percentage of chlorine in chloroprene yielded low results due to loss by volatilization. (The sample of chloroprene was supplied by Ira Williams of the Jackson Laboratory, E. I. du Pont de Nemours & Co.)

5. If the substance analyzed is crystalline, difficultly soluble in alcohol, and highly refractory chemically, the fineness of division is extremely important to the success of the analysis. In the earlier literature divergent results for hexachlorobenzene and benzene hexachloride were reported. Similar difficulties were encountered in the authors' analysis of tetrachlorobenzene. These discrepancies were probably due to the state of division of the sample and also to insufficient refluxing with the reducing media. In such cases it was found necessary to increase the quantities of sodium and alcohol employed to twenty per cent over those proposed by Drogin and Rosanoff, and to extend the time of heating to 2 hours after addition of the last portion of sodium.

6. In all analyses, filtration of the precipitated silver halide is necessary. Should the filtrate produce interfering colors on the addition of indicator solution, the analysis must be repeated, with the excess of precipitant determined gravimetrically (as silver chloride). In all analyses reported herein, the Volhard procedure was employed.

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Improved Laboratory Screw Clamp

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As the ordinary laboratory screw clamp is equipped with a small, narrow screw head, the thumb and fingers of the operator often suffer injury when frequent tightening or adjusting is performed. It is often necessary to use pliers to open or close this type of clamp, especially if used on pressure tubing or when the screw has become corroded. This prompted the writer to provide the clamp with an enlarged knurled head, having a broader gripping surface and a greater diameter. This also simplifies fine adjustment when the clamp is used for regulating the flow of gases or liquids through rubber tubing.

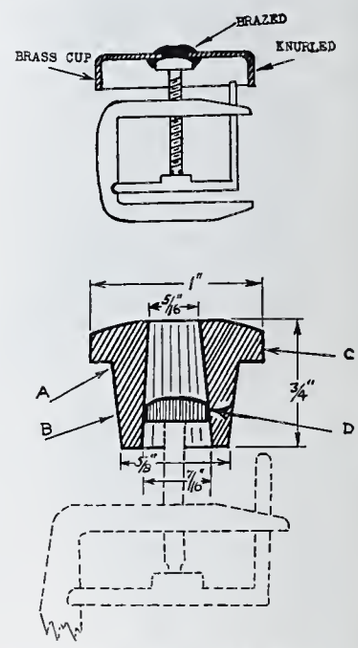

Figure 1. Methods for Improving Efficiency of Laboratory Screw Clamps

A, stainless steel. *B*, screw head gripped by lands and grooves. *C*, knurled. *D*, interior taper, 1 on 10, with 24 lands and grooves 0.031 inch deep.

The device tried first consisted merely of a new screw, with enlarged head, turned from solid rod. This was soon replaced by simply brazing a knurled brass cup of the appropriate depth and diameter to the original screw head. The brazing was accomplished through a small hole in the center of the cup and when properly executed gives a strong union.

A more convenient device is the auxiliary head turned from stainless steel and given a set of triangular "lands and grooves" as elements of the interior taper. This steel head is driven onto the screw head of the customary clamp, the "lands" biting into the brass and effecting a secure hold. Since screw clamps are of inexpensive construction and are ordinarily short-lived, this head may be removed and used again when the clamps are discarded.

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Chlorine Determination in Coal

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THE determination of chlorine in coal has received but little attention from coal chemists. In connection with their investigation of formulas for calculation of the amount of mineral matter in coal, Parr and Wheeler (*2*) determined chlorine in a number of Illinois coals by digesting pulverized coal with water and titrating with standard silver nitrate solution (Mohr's method). From 0.0 to 0.56 per cent of chlorine was found in the coals tested. Dunningham (*1*) mentions the probability of relatively large amounts of chlorine causing corrosion in boiler furnaces and economizers. For a number of British coals he shows analyses of chlorine ranging from a trace up to 1.00 per cent chlorine as determined by the Carius method. In the ceramic industry high-chlorine coals are considered undesirable for the firing of unglazed clay products because of the glazing action of volatile alkali chlorides.

The tests described in this paper show that extraction of pulverized coal with water may give results much too low for chlorine. A simple method is proposed whereby the organic coal substance is destroyed by ignition in an oxygen-bomb calorimeter and chlorine is determined in the bomb washings.

Volhard's volumetric method for determination of chlorine, used in the tests described herein, includes any bromine or iodine that may be present in the coal. There appear to be no published data concerning the amount of bromine occurring in various coals. Wilke-Dörfurt and Römersperger (*3*) determined the iodine content of twelve European coals and found from 0.85 to 11.17 mg. of iodine per kg. of coal. The largest amount found would correspond to only 0.001 per cent of the coal.

Experimental Data

Twelve bituminous coals from Illinois, Indiana, West Virginia, Pennsylvania, Ohio, and Oklahoma were selected. The samples were pulverized to pass a 60-mesh sieve. For the water-extraction method 4-gram samples were used, except for the Oklahoma coal where 1-gram samples were taken on account of its high chlorine content. For the bomb-washing method, which is described later, the coal was burned in increments of 1 gram, except in the case of the high-chlorine Oklahoma coal where 0.5-gram samples were used.

In the water-extraction method, 4 grams of 60-mesh coal were wetted by shaking with 75 cc. of water in a stoppered Erlenmeyer flask, after which 5 cc. of nitric acid (1 to 5) were added. A short-stem funnel was inserted into the top of the flask and the contents boiled gently for one-half hour, then filtered and washed thoroughly. The filtrate was evaporated to a volume of approximately 100 cc. Volhard's method, described in the procedure for the bomb-washing method, was used for the determination of chlorine, and was found to be more suitable than Mohr's method, in which the water extraction is titrated for chlorine with silver nitrate. Some coals, especially if weathered, contain a sufficient quantity of iron sulfate to interfere with the end point in Mohr's method.

Table I shows that the bomb-washing method gives consistently higher results for chlorine than does the water-extraction method, which is apparently not reliable, as it is likely to give much too low results. It is of interest to note that the differences between the two methods for the coal tested from Illinois, Indiana, and Ohio are relatively small, whereas large differences are shown for the coals tested from Oklahoma, West Virginia, and Pennsylvania.

Tests were made to determine whether finer grinding of the samples would give higher results in the water-extraction method, as well as to determine the effect of longer digestion and of better wetting of the coal particles by lowering the surface tension of the water by means of alcohol. The water-alcohol mixture used contained 25 per cent ethyl alcohol. Table II gives the results of these additional tests, and shows (1) that fine grinding of the coal increased the amount of chlorine extracted, (2) that prolonged digestion increased the chlorine extracted, and (3) that more chlorine was extracted by means of the water-alcohol mixture than by water alone. In the tests in which the water-alcohol mixture was used the digestion flasks were provided with water-cooled condensers. A comparison of the results obtained with chlorine determined by means of the bomb-washing method shows that in all cases the chlorine values by the extraction methods are too low.

Additional tests were made to determine the chlorine remaining in the residue from the water-extraction method.

Table I. Chlorine in Coal as Determined by Water-Extraction and Bomb-Washing Methods

Source of Coal			Laboratory Number	Volhard Water-Extraction Method		Bomb-Washing Method		Bomb-Washing Method Compared to Water-Extraction Method
State	County	Bed		Individual determinations	Average	Individual determinations	Average	
				%	%	%	%	%
Illinois	Marshall	No. 7	A45464	0.106		0.108		
				0.105	0.106	0.110	0.109	+0.003
Illinois	Will	No. 2	A52979	0.007		0.009		
				0.007	0.007	0.006	0.008	+0.001
Illinois	Marshall	No. 7	A45318	0.028		0.027		
				0.028	0.028	0.028	0.028	0.000
Illinois	Jackson	No. 6	A48815	0.010		0.013		
				0.010	0.010	0.011	0.012	+0.002
Indiana	Knox	No. 4	A57483	0.058		0.061		
				0.058	0.058	0.062	0.062	+0.004
West Virginia	Preston	Bakerstown	A28925	0.022		0.184		
				0.022	0.022	0.180	0.182	+0.160
West Virginia	Ohio	Pittsburgh	A32387	0.028		0.072		
				0.028	0.028	0.074	0.073	+0.045
West Virginia	Boone	Alma	A74397	0.038		0.247		
				0.037	0.038	0.242	0.245	+0.207
Pennsylvania	Jefferson	Lower Freeport	A34491	0.020		0.140		
				0.020	0.020	0.135	0.138	+0.118
Pennsylvania	Indiana	Upper Freeport	A72831	0.023		0.176		
				0.021	0.022	0.180	0.178	+0.156
Ohio	Jackson	Sharon	A66308	0.009		0.012		
				0.008	0.009	0.012	0.012	+0.003
Oklahoma	Okmulgee	Henryetta	A68380	0.209		0.459		
				0.208	0.209	0.461	0.460	+0.251

Table II. Effect of Fineness of Sample, Time of Digestion, and Use of Water-Alcohol Mixture on Determination of Chlorine by Volhard Water-Digestion Method

Laboratory Number	Time of Digestion	Fineness of Sample, Mesh	Chlorine Extracted: Water-Extraction, Individual determinations	Water-Extraction, Average	Water-Alcohol Mixture, Individual determinations	Water-Alcohol Mixture, Average	Bomb-Washing Method
	Hours		%	%	%	%	%
A74397	0.5	60	0.038		0.049		
			0.037	0.038	0.044	0.047	0.245
A74397	0.5	200	0.044		0.059		
			0.044	0.044	0.060	0.060	...
A74397	0.5	325	0.077		0.095		
			0.078	0.078	0.094	0.095	...
A74397	4	325	0.128		0.143		
			0.125	0.127	0.146	0.145	...
A72831	0.5	60	0.023		0.033		
			0.021	0.022	0.034	0.034	0.178
A72831	0.5	200	0.029		0.043		
			0.031	0.030	0.044	0.044	...
A72831	0.5	325	0.046		0.062		
			0.044	0.045	0.059	0.061	...
A72831	4	325	0.073		0.087		
			0.075	0.074	0.091	0.089	...

Samples of 60-mesh coal were extracted for one-half hour at boiling temperature by the water-extraction method and chlorine was determined in the filtrate by Volhard's method. The residues were then burned in an oxygen bomb and chlorine determined in the bomb washings. The sum of the chlorine extracted by water and the chlorine in the residues should comprise the total chlorine of the coal and agree with the chlorine as determined in the original coal by the bomb-washing method. Table III gives the results of these tests and shows that relatively large amounts of the chlorine of some coals cannot be dissolved by extraction with water. The sum of the chlorine as determined by water extraction and that remaining in the residue agree satisfactorily with the total chlorine as determined in the original coal by the bomb-washing method, which method is recommended for the determination of chlorine in coal.

Table III. Chlorine in Residues from Volhard Water-Extraction Method

Laboratory Number	Volhard Water-Extraction Method: Individual determinations	Volhard Water-Extraction Method: Average	Bomb-Washing Method: Residues from Water-Extraction Method: Individual determinations	Residues from Water-Extraction Method: Average	Sum of Water-Extractable Chlorine plus Chlorine in Residue	Chlorine in Original Coal, as Determined by Bomb-Washing Method
	%	%	%	%	%	%
A45464	0.105		0.009			
	0.104	0.105	0.007	0.008	0.113	0.109
A52979	0.008		0.002			
	0.007	0.008	0.002	0.002	0.010	0.008
A45318	0.026		0.007			
	0.025	0.026	0.008	0.008	0.034	0.028
A48815	0.012		0.003			
	0.011	0.012	0.002	0.003	0.015	0.012
A57483	0.058		0.002			
	0.056	0.057	0.004	0.003	0.060	0.062
A28925	0.023		0.169			
	0.020	0.022	0.164	0.167	0.189	0.182
A32387	0.030		0.046			
	0.028	0.029	0.043	0.045	0.074	0.073
A74397	0.034		0.215			
	0.035	0.035	0.219	0.217	0.252	0.245
A34491	0.016		0.116			
	0.017	0.017	0.119	0.118	0.135	0.138
A72831	0.024		0.161			
	0.022	0.023	0.156	0.159	0.182	0.178
A66308	0.008		0.001			
	0.008	0.008	0.001	0.001	0.009	0.012
A68380	0.210		0.257			
	0.207	0.209	0.255	0.256	0.465	0.460

Bomb-Washing Method for Chlorine Determination

A Parr oxygen bomb of illium metal was used for the chlorine determinations. Other types of oxygen bombs are equally satisfactory if they have inner surfaces which are not attacked by the products of combustion.

Place about 0.5 cc. of distilled water in the bottom of the bomb to saturate with moisture the oxygen used for combustion. Put a 1-gram sample of coal (60-mesh) in a platinum tray, the bottom of which is covered with fused alumina (alundum). Connect a short length of iron wire of about No. 34 B. & S. gage across the terminals of the bomb to ignite the coal. Fill the bomb with oxygen to a pressure of about 30 atmospheres and submerge in water in the calorimeter bucket. Fire the charge electrically and allow the bomb to stand in the calorimeter water for not less than 5 minutes after firing.

Remove the bomb from the calorimeter water and open the valve carefully to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 minute. The bomb should be provided with a device for controlling the valve so as to permit a slow and uniform release of the gases. Wash all parts of the interior of the bomb, including the tray, with a fine jet of distilled water. It is essential to wash through the valve opening also, as considerable spray may collect in this opening.

Collect the washings in a beaker, filter, and wash the filter paper with hot distilled water. Evaporate the washings to about 100 cc. and add 5 cc. of dilute nitric acid (1 to 5). Add standard silver nitrate solution to about 2 cc. in excess and warm, with frequent stirring, until the silver chloride precipitate coagulates. Allow to cool in the dark, filter, and wash with distilled water containing 1 per cent by volume of nitric acid. Add 5 cc. of nitric acid (1 to 1) and 4 cc. of ferric ammonium sulfate as an indicator, and titrate the excess silver nitrate with standard ammonium thiocyanate solution until a faint pink persists after vigorous stirring. All the nitric acid used in the method should first be boiled until colorless to remove lower oxides of nitrogen.

Make a blank determination covering the entire procedure as described. The blank determinations were found to be low, averaging about 0.1 cc. of the standard silver nitrate solution.

For some coals the chlorine is so low that it is advisable to burn more than 1 gram of coal. In such cases the coal is burned in increments of 1 gram. One blank determination multiplied by the number of burnings of coal will suffice for the blank correction in such cases. The amount of coal to be burned in order to give satisfactory results is as follows.

Chlorine %	*Grams*
Over 0.4	0.5
0.4–0.1	1
0.1–0.05	2
Under 0.05	4

Solutions Used

1. 4.79 grams of silver nitrate, water to make 1 liter.
2. 2.2 grams of ammonium thiocyanate, water to make 1 liter.
3. 16.48 grams of pure fused sodium chloride, water to make 1 liter. Dilute 100 cc. of this stock solution to 1 liter, then 1 cc. is equivalent to 0.001 gram of chlorine.
4. Cold saturated solution of ferric ammonium sulfate. Add 5 cc. of nitric acid (1 to 1) per 100 cc. of solution. The nitric acid used should be boiled until colorless.

To standardize the ammonium thiocyanate in terms of silver nitrate take 100 cc. of water, add 5 cc. of recently boiled nitric acid (1 to 1) and 4 cc. of ferric ammonium sulfate indicator. Add a measured amount of silver nitrate solution (4 to 6 cc.) and titrate with ammonium thiocyanate.

To standardize the silver nitrate in terms of chlorine add 5 to 8 cc. of the standard sodium chloride solution to 100 cc. of water containing 5 cc. of recently boiled nitric acid

(1 to 5). Add an excess of about 2 cc. of the silver nitrate solution, and determine the excess of silver nitrate according to the procedure described for the bomb-washing method. Calculate the strength of the silver nitrate solution in terms of chlorine.

ACKNOWLEDGMENT

This investigation of the bomb method was made at the suggestion of A. C. Fieldner, chief engineer, Experiment Stations Division, U. S. Bureau of Mines.

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Determination of Plasticizers in Organic Cellulosic Plastics

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IN RECENT years where greater stability and lower flammability of plastic compositions have been sought, organic esters and ethers of cellulose have replaced cellulose nitrate to a considerable extent. Frequently, practical workers in the field of plastics are confronted with the analysis of these newer cellulosic compositions and the methods employed have been largely those which have proved timeworthy in the realm of cellulose nitrate plastics. Many of the methods (*2*) used in the analysis of pyroxylin (cellulose nitrate) plastic are basically founded upon the recognition that the major component is unstable at elevated temperatures. By taking advantage of the greater temperature stability of the organic derivatives of cellulose, it has been found possible greatly to expedite and simplify the analysis of such plastics.

TABLE I. DETERMINATION OF PLASTICIZER CONTENT OF CELLULOSE DERIVATIVE PLASTICS

Plastic Analyzed[a]	Plasticizer Content Present	Found	Difference
	%	%	%
Cellulose acetate, Type A	41.2	40.6	0.6
Cellulose acetate, Type B	41.2	40.5	0.7
Cellulose acetate, Type C	41.2	41.0	0.2
Cellulose acetate, Type D	28.6	28.3	0.3
Cellulose acetate, Type E	47.4	46.9	0.5
Ethyl cellulose, Type A	33.3	32.7	0.6
Ethyl cellulose, Type B	33.3	32.9	0.4
Benzyl cellulose, Type A	13.0	12.8	0.2
Benzyl cellulose, Type B	11.1	11.0	0.1

[a] In order to prove that the method possesses wide application, the plastic samples analyzed were made from different plasticizers and different kinds of cellulose derivative. The cellulose derivatives varied in chemical properties (acetyl content, ethoxy content, etc.), or physical properties (melting point, viscosity, etc.).

Of primary significance to the plastic chemist is the determination of the character of the cellulose derivative and the amount as well as chemical nature of the plasticizer used. As in the case of lacquers (*1*), these determinations are usually conducted by dissolving the plastic in a suitable low boiling point solvent and subsequently precipitating the cellulose derivative by addition of a low boiling point nonsolvent for the cellulose derivative which is a solvent for the plasticizer. The precipitated cellulose derivative is filtered, washed, and dried. The filtrate is concentrated by distillation to remove the low boiling point solvents, leaving a still residue which constitutes the plasticizer. In general, this method is satisfactory for the separation of the cellulose derivative, although it is frequently necessary to employ great dilutions or repeat the precipitation to obtain the cellulose derivative in the pure state.

However, for the rapid determination and identification of plasticizers, the precipitation method as outlined becomes extremely burdensome. Frequently, plastic compositions contain a mixture of plasticizers and the use of large samples greatly aids the separation of the mixture into its components. To separate large amounts of the plasticizer from the plastic by the precipitation method requires large volumes of costly solvents and the operations are time-consuming. In order to circumvent these difficulties, the following method of separation was devised.

PROCEDURE

Five hundred grams of plastic material cut into small strips are placed in a 2-liter distilling flask equipped with a thermometer and the flask immersed in an oil bath almost to the side arm; or if preferred, the neck of the distilling flask may be wrapped with asbestos cord. A receiving flask of 500 cc. capacity is attached to the side arm of the flask and kept cool by immersion in a freezing mixture or by other suitable means. A vacuum of 0.1 mm. of mercury is applied to the system and the oil bath rapidly heated. The analysis of a number of plastic compositions made from cellulose acetate, ethyl cellulose, benzyl cellulose, and plasticizers of different types led to the adoption of an oil bath temperature of 250° to 260° C. This temperature, while resulting in a slight charring, did not produce any appreciable amount of volatile decomposition products of the cellulosic material, yet it was found sufficiently high to effect distillation of the high boiling plasticizers in common usage. Lower temperatures, while satisfactory if the plasticizer is not characterized by too high a boiling point, unnecessarily prolong the time of separation. Higher temperatures produce volatile decomposition products of the cellulosic material, which, however, are usually easily removable by the customary methods of purification. Using an oil bath temperature of 250° to 260° C., a complete separation may be carried out in a few hours. When separation is completed, which is indicated by the fact that distillate no longer collects in the receiving flask, the contents are redistilled in the usual way or by the method of Hickman and Sanford (*3*).

DISCUSSION

Samples of ethyl cellulose, benzyl cellulose, and cellulose acetate plastics were analyzed by the above procedure. The results obtained are outlined in Table I. In all cases, the

purity of the plasticizer was determined by refractive index measurements, as well as by saponification values if the plasticizer belonged to the ester type.

Summary

A rapid method for the separation of plasticizers from organic cellulosic plastics, described in this article, has been shown to be applicable to ethyl cellulose, benzyl cellulose, and cellulose acetate plastics.

Its accuracy, when applied quantitatively to the determination of plasticizer content of organic cellulosic plastics, was found satisfactory for practical purposes.

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Preparation of Sodium Hydroxide Solutions of Low Carbonate Content by Centrifugation

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Having had occasion to prepare sodium hydroxide solutions of low carbonate content, the use of a centrifuge in connection with the oily alkali method (*6*) suggested itself. This method has long been used for preparing sodium hydroxide solutions and possesses the advantages of simplicity and freedom from the introduction of contaminating ions. On the other hand it has the disadvantages of extreme slowness and incomplete removal of carbonate. Clark (*1*) speeded up the process by filtering the alkali through paper, and Kolthoff (*4*) filtered it through a Jena sintered-glass crucible. Han and Chao (*2*), who have recently made a comprehensive study of all methods of preparing alkali free from carbonate, clarified the solution by heating in a water bath (*5*) and followed this by filtration through glass. Apparently no one has made use of the centrifuge for the clarification.

Experimental

Samples of the oily alkali were prepared by dissolving 50 grams of pellet sodium hydroxide in 50 ml. of carbon dioxide–free water. After cooling, each lot was transferred to a Pyrex centrifuge tube, made from a 125-ml. Erlenmeyer flask by rounding out the base and blowing out an opening to fit a No. 2 rubber stopper. The neck of the flask was drawn off and a tube 5 cm. long and 0.8 cm. inside diameter sealed on. Centrifuging for 30 minutes at 2200 to 2300 r. p. m. gave absolutely clear solutions with the undissolved carbonate and alkali tightly packed in the bottom.

Table I. Carbonate Content of Alkali

Sample	Total Vol. Acid as 0.0998 *N* HCl	Vol. HCl for CO_3^{--}	Per Cent HCl for CO_3^{--}
	Ml.	*Ml.*	
	before centrifuging		
1	273.36	2.40	0.88
2	270.67	2.42	0.89
3	306.66	2.48	0.81
4	275.24	2.26	0.82
	after centrifuging		
1	271.28	0.314	0.12
	278.37	0.284	0.10
2	309.35	0.510	0.16
3	276.33	0.280	0.10
4	330.64	0.450	0.14
			Av. 0.12

Samples of alkali were analyzed for carbonate before and after centrifuging by titration in the absence of carbon dioxide with standard hydrochloric acid. On reaching a phenolphthalein end point the titration was continued with 0.0998 *N* hydrochloric acid, from a microburet, to a pH of 4.2 as determined by methyl orange indicator and a buffer solution. The natural offset between the two end points for pure water was found to be 0.140 ml. and this correction was applied. Some typical data are given in Table I.

Discussion of Results

Han and Chao (*2*) secured an average value of 0.15 per cent for the hydrochloric acid used for the carbonate in their solutions, whereas the above data show an average of 0.12 per cent for the centrifuged alkali. This clearly indicates that centrifugation gives a lower content of carbonate in the alkali with a very much smaller expenditure of time and labor. Then, too, no elaborate heating or filtering devices are needed.

Forty milliliters of a 0.1124 *N* sodium hydroxide solution prepared by diluting the centrifuged alkali with carbon dioxide–free water required an average of 0.190 ml. of 0.0998 *N* hydrochloric acid to go from the phenolphthalein end point to pH 4.2. This value less 0.140 ml. (the natural offset) equals 0.050 ml., which corresponds to the carbonate content. Solutions prepared in this manner are perfectly satisfactory for all ordinary titrations.

Modified Titration Head

In connection with the above work the titration head recommended by Hillebrand and Lundell (*3*) has been modified by leading the carbon dioxide–free air stream through a tube passing through the cap by a ring seal and extending down about 8 cm. below the top of the head. This change insures that the titration flask will be completely swept out by the air stream. The head was made of very heavy Pyrex tubing and of a size to fit over a 250-ml. Erlenmeyer flask. Such a titration head makes a very rugged and useful piece of equipment.

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Precise Automatic Apparatus for Continuous Determination of Carbon Dioxide in Air

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In view of the important role of atmospheric carbon dioxide in many phases of biology, such as animal and plant respiration, photosynthesis, and air pollution, it is surprising that no adequate method has thus far been proposed for determining it continuously and automatically. The best methods are somewhat laborious and time-consuming, and have an admitted uncertainty of 5 to 10 parts per million. This applies to the gasometric method of Sondén as employed by Benedict (*1*), the Pettenkofer evacuated-bottle method of Johnston and Walker (*4*), and the electrometric method of Spoehr and McGee (*8*). Even though these methods may indicate the total concentration of the gas in the air with sufficient precision for many purposes, they leave much to be desired—except under special conditions of operation—when they are applied to the problem of measuring small differences of concentration at two points in an air stream in order to evaluate the amount of carbon dioxide absorbed or evolved in an experiment. While this paper was being prepared for publication, articles by Heinicke and Hoffman (*3*) and Martin and Green (*6*) appeared. These methods, which are more promising than the others on account of their high rate of aspiration, will be referred to again below.

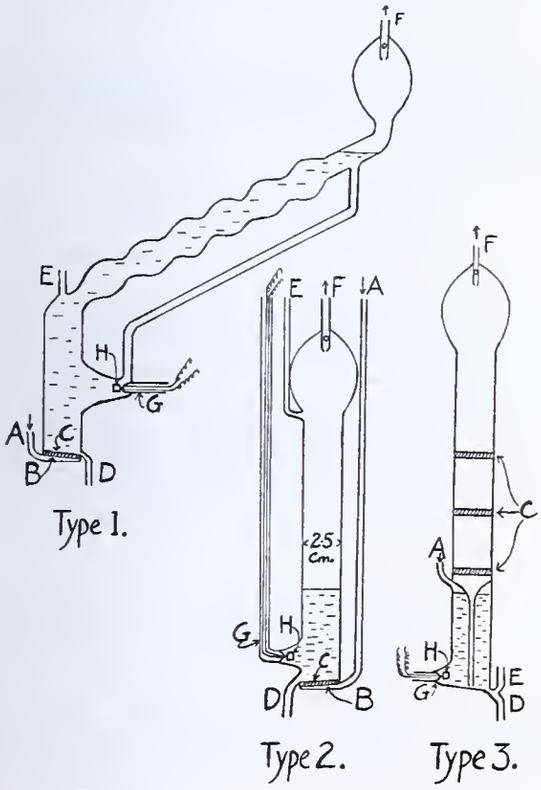

Figure 1. Types of Absorbers

With the development of the author's automatic apparatus for the determination of small concentrations of sulfur dioxide in air (*9, 10, 11*), it became clear that a similar machine applicable to the determination of atmospheric carbon dioxide would be useful in studies of the action of sulfur dioxide on vegetation. Such a carbon dioxide autometer would make possible direct observations without mechanical interference of rates of photosynthesis and respiration in plants—processes which are fundamental to metabolism and growth—and would thus afford an immediate quantitative measure of the effect of many types of experimental treatment. The apparatus should also be particularly useful in animal respiration studies because measurements could readily be made under a wide range of conditions.

The modification of the laboratory model of the sulfur dioxide autometer (*9*) was accordingly undertaken in the hope of producing a machine which would measure continuously and automatically the carbon dioxide concentration at intake and outlet of fumigation chambers, thus determining the amount of gas absorbed or evolved by the experimental plants in the chamber. A few preliminary observations made it clear that the principal problem to be solved was the development of an efficient absorber for carbon dioxide, which unlike sulfur dioxide, is very difficult to remove from a rapid air stream, unless one uses a solid absorbent. With a liquid absorbent in an ordinary bubbler, strong alkali and low rates of aspiration are necessary to absorb all the gas. For example, Spoehr and McGee (*7*) used 60 to 125 ml. of 0.1 *N* barium hydroxide in a 10-bulb Pettenkofer tube, to effect absorption from an air stream of about 6 cc. per minute.

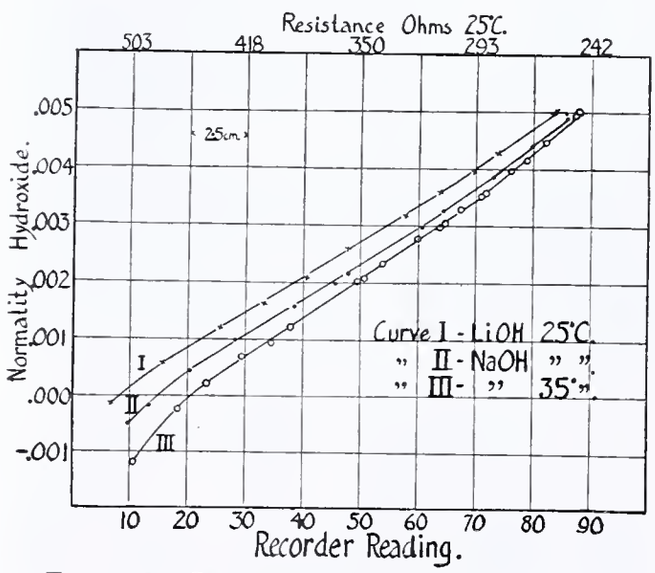

Figure 2. Calibration Chart of Absorbers

Resistance of 0.0052 *N* alkali solutions as indicated by a recording Wheatstone bridge, at different stages in conversion of hydroxide to carbonate. Positive values of hydroxide concentration represent mixtures of hydroxide and carbonate; negative values represent mixtures of carbonate and bicarbonate.

The spiral absorber of Martin and Green (*6*), recently described, absorbs all the carbon dioxide from an air stream of 333 cc. per minute (20 liters per hour) in 30 ml. of 0.07 *N* barium hydroxide. Unfortunately the efficiency of this absorber falls rapidly as the concentration of the alkali is reduced. Since the atmosphere contains only 0.3 cc. of carbon dioxide per liter, it was evident that an absorber was necessary which could handle moderate volumes of air (several hundred cubic centimeters per minute) with hy-

droxide of strength preferably less than 0.01 *N* in order that appreciable changes in the solution might be produced in short time periods (2 minutes).

Absorption Apparatus

A consideration of the problem indicated that it would be necessary to produce very small bubbles in the absorbing liquid in order to attain high efficiency for the apparatus, and for this purpose the use of fritted glass disks seemed promising. The commercial bubblers made of Jena glass were too coarse, and the finer Jena disks were not mounted in apparatus suitable for the purpose in hand. It was suggested to the writer in private conversation by R. A. Fulton of the U. S. Bureau of Entomology, Twin Falls, Idaho, that fritted glass disks could readily be made of Pyrex glass; and later the note of Bruce and Bent (*2*) on this subject was found. Accordingly a number of different types of absorbers were constructed of Pyrex glass, utilizing disks of different porosities. Figure 1 shows three of these absorbers.

Types 1 and 2, with porous plates made of 150- to 200-mesh glass, had an efficiency of about 60 per cent with air streams of 200 to 300 cc. per minute and alkali of about 0.005 to 0.01 *N*. Type 3 was constructed with 3 disks made from glass powder of 100 to 150 mesh. This absorber had an efficiency of 80 to 85 per cent under similar conditions of operation. With 0.1 *N* alkali, the efficiency was raised to about 90 per cent in types 1 and 2, and 95 per cent in type 3.

These gas distributors produced bubbles of an order of about 0.5 mm. in diameter, but offered considerable resistance to the gas stream, suction of 5 to 10 cm. of mercury being necessary to draw the gas sample through them. It was evident, therefore, that increased efficiency could not be sought with disks of finer pores on account of the mechanical difficulty of drawing the gas through the septum.

It is well known, as pointed out by Maier (*5*), that the size of the bubble is a function not only of the diameter of the orifice from which the gas emerges, but also of the surface tension of the liquid. It was therefore decided to add a surface tension depressant to the absorbing liquid. For this purpose the higher alcohols suggested themselves as being particularly suitable because they produce large depressions with low concentrations and because they do not affect the conductance of the system. Normal butyl alcohol was used in amounts ranging from 0.1 to 2 per cent, depending on the porosity of the fritted glass disks and the rate at which the gas was to be aspirated. The addition of the surface tension depressant not only reduced the size of the bubbles, but also produced a froth which increased the time of contact of the gas with the liquid. In fact, the apparent volume of the liquid phase was increased two or three times, and the tiny bubbles circulated around in the system, many of them rising to the top and returning to the bottom before finally emerging from the top of the liquid-air mixture. This frothing action, together with the smaller bubbles, raised the efficiency of all the absorbers to 100 per cent with 0.005 *N* alkali. Further, the resistance of the septum to the passage of gas was reduced somewhat by the alcohol.

The absorber type 2, Figure 1, the form finally chosen, was designed to hold 30 to 60 ml. of solution. It was provided with an intake tube, *A*, and a very small chamber, *B*, below the 22-mm. fritted glass septum, *C*. Chamber *B* was made as small as possible, about 0.5 to 1.0 cc. capacity, in order to minimize the trapping of liquid below the septum when the vessel was emptied through *D*. The absorber was provided with a tube for adding the liquid, *E*, and the outlet, *F*. All tubes extended above the absorber so that the vessel could be completely immersed in a water thermostat. The conductivity electrodes, *H*, were made by welding electrically in an inert atmosphere a piece of platinum foil around the end of a tungsten wire, then welding a platinum plate to the platinum tip. A pair of plates, suitably spaced, were sealed in a small glass tube, *G*, and mounted in the absorber. If the electrodes were of considerable size, a supporting glass bead was inserted between them.

The measurement of the carbon dioxide absorbed was based on the fact that the conductance of a carbonate solution is only about half that of the hydroxide solution of the same concentration.

Efficiency of Absorption

The efficiency of the absorbers was determined as follows:

Two vessels were mounted in an accurately controlled water thermostat, and air, measured in a gas meter, was drawn through them in series. At 2-minute intervals the aspiration was stopped and the conductance of the two solutions measured with a recording Wheatstone bridge. The absorbing liquid was 0.005 *N* sodium hydroxide and the resistance of the bridge had a range from 230 to 550 ohms, so that it was possible to read the resistance of the solution to within about 0.3 ohm. This precision was sufficient to detect with certainty losses from the first absorber as small as 1 per cent of the carbon dioxide in each 2-minute sample.

The results of this study are summarized in Table I, which gives the efficiency of the first absorber in percentage, with different rates of aspiration and different concentrations of carbon dioxide in the air and also with different amounts of normal butyl alcohol in the absorbing liquid. The efficiencies are shown at different stages in the conversion of hydroxide to carbonate and bicarbonate. An accumulated efficiency is the

Table I. Efficiency of Absorber as Influenced by Rate of Air Flow, Concentration of Carbon Dioxide in Air, and Amount of Butyl Alcohol, with 0.0052 *N* NaOH, at Different Stages in Conversion of Hydroxide to Carbonate or Bicarbonate

Rate of Air Flow	CO_2 in Air	Volume of Absorbing Solution	Efficiency of Absorption at Average Hydroxyl Normalities									
			0.0045	0.0040[a]	0.0035	0.0030	0.0025	0.0020	0.0010	0.0000[b]	−0.0010	−0.0020[c]
Cc./min.	*P. p. m.*	*Ml.*	%	%	%	%	%	%	%	%	%	%
					0.1 per cent butyl alcohol							
170	820	35	100	100	100	100	100	96	..	93	90	
280	920	37	100	100	...	98	98	97	96	93	91	88
280	1100	35	100	...	100	..	96	..	96	91	86	77
330	900	31	100	100	100	98	98	97	..	92	87	87
340	900	37	...	98	98	96	96	96	93	91	..	88
315	340	34	100	...	99	98	96	98	96	94	91	..
340	320	35	100	100	98	98	98	98	98	94	90	85
355	330	50	100	100	100	100	98	98	98	96	94	..
440	380	50	100	100	100	99	99	..	97	95	92	83
460	530	50	100	...	100	98	97	97	97	97	93	..
					0.4 per cent butyl alcohol							
204	610	35	100	...	100	100	100	100	100	100	99	95
330	320	35	100	100	100	100	100	100	98	100	98	94
330	520	37	100	...	100	..	...	100	99	95	95	..
370	410	31	100	100	100	100	99	98	94	92	87	..
440	320	40	100	...	100	..	98	98	97	93	89	81
500	740	40	...	96	...	96	...	93	..	80	63	..

[a] 0.0040 NaOH + 0.0012 Na_2CO_3.
[b] 0.0052 Na_2CO_3.
[c] 0.0032 Na_2CO_3 + 0.0020 $NaHCO_3$.

average of the values to a chosen stage of the process. The data indicate that if sufficient alcohol was present, the absorber did not begin to allow carbon dioxide to pass until practically all the hydroxide was converted into carbonate, when the rate of aspiration was less than about 350 cc. per minute. The efficiency was still about 80 per cent when 40 per cent of the alkali was converted to bicarbonate. The same results were obtained with air containing three times the normal amount of carbon dioxide. At 450 cc. per minute, however, the solution began to allow carbon dioxide to pass when about half of the hydroxide was changed to carbonate. In other experiments, not recorded in Table I, an efficiency of 98 per cent was observed with velocities of 700 cc. per minute, using 25 ml. of 0.1 *N* alkali and 0.4 per cent butyl alcohol as the absorbent. Evidently the absorber can be used with 0.005 *N* alkali and velocities up to about 350 cc. per minute with practically 100 per cent efficiency of absorption until nearly all the hydroxide is changed to carbonate. It should be noted, however, that the efficiency decreased when the velocity was too low to produce froth in the solution. For example, in one experiment, at 30 cc. per minute without any foaming, 10 per cent of the carbon dioxide escaped, whereas it was all absorbed at 300 cc. per minute.

Table II. Efficiency of Absorption of Carbon Dioxide by 250 cc. 0.1 $Ba(OH)_2$ in Absorber Similar to That Described by Heinicke and Hoffman

Rate of Air Flow	Height of Column Liquid	Height of Column Froth	Surface Tension	Efficiency of Absorption
Cc./min.	*Cm.*	*Cm.*	*Dynes/cm.*	%
320	30	0.5	72	100
850	30	5	72	97
2200	30	30	72	93
2200	30	60	63	96

Heinicke and Hoffman (*3*) claim that all the carbon dioxide can be removed from an air stream of 1670 cc. per minute (100 liters per hour) in a large absorber tube containing 200 ml. of 0.1 *N* barium or potassium hydroxide, and provided at the bottom with a 30-mm. fritted glass septum of 100- to 120-micron pore diameter. Table II shows that while this claim could not be strictly confirmed, the method is very promising. The absorber was similar to that of Heinicke and Hoffman, except that it had a 30-mm. Jena G 2 filter of 40- to 50-micron rated pore diameter and contained 250 ml. of 0.1 *N* barium hydroxide. The high efficiency at the maximum velocity employed, which could be further improved by the addition of a surface tension depressant, indicates that a considerable range of velocities of aspiration is possible if desired. Evidently the success of Heinicke and Hoffman's absorber (*3*) is due in part to the formation of considerable foam even without a surface tension depressant.

Hydroxide Solution

From a consideration of the transport numbers of lithium and sodium hydroxide it was assumed that lithium hydroxide would show a greater change of conductance on being converted into carbonate than would sodium hydroxide, and much of the earlier work with the method was carried out with lithium hydroxide. However, as the calibration curves in Figure 2 show, the difference in behavior between these two alkalies is so small that one has no appreciable advantage over the other. Accordingly sodium hydroxide is now being used. Barium hydroxide might be used as the absorbent, in which case a much larger change of conductance would be observed on the addition of carbon dioxide to the solution because of the precipitation of barium carbonate. Experiments with barium hydroxide, however, indicated that while the presence of the precipitate did not affect the measurement of the conductance appreciably, especially if the absorbing vessel was cleaned occasionally with dilute hydrochloric acid, a serious

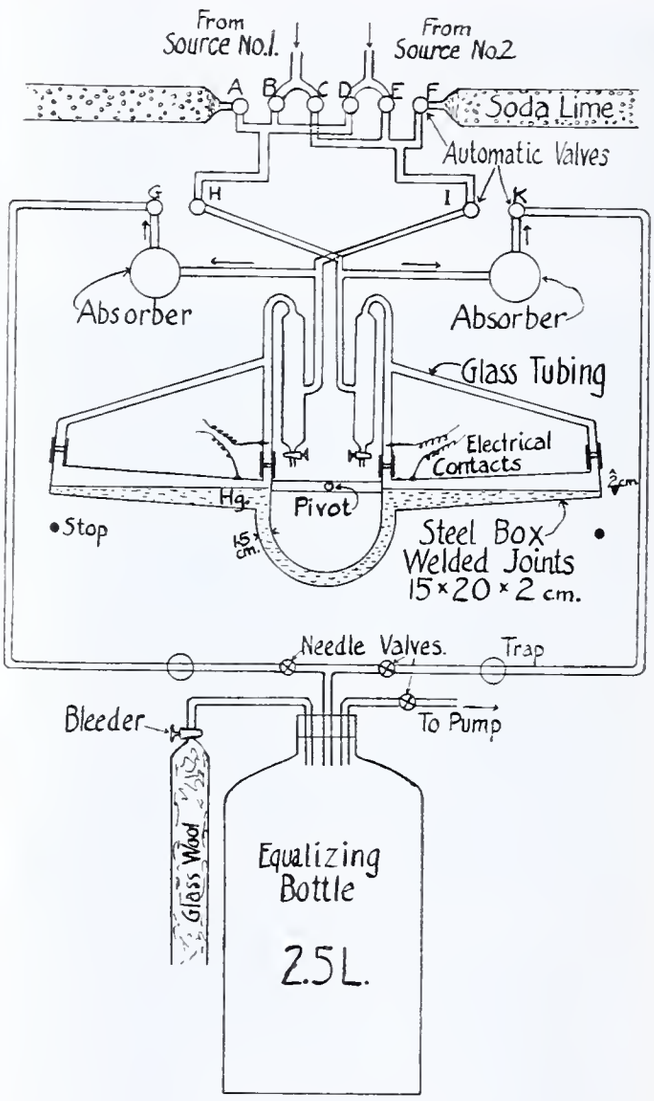

Figure 3. Diagram of Air-Flow Control System

Showing method of alternating source of air sample (top); steel gas meter and absorbers (center); and surge bottle and control valves (bottom).

disadvantage was incurred because of the fact that the conductance of the solution decreased slowly for about half an hour after precipitation occurred. Apparently the solubility of barium carbonate was decreasing during this time, presumably because of growth in the size of the particles of the precipitate. The fact that equilibrium measurements could not be made quickly with barium hydroxide rendered that absorbent practically worthless for the purpose at hand.

Calibration of Electrodes

The problem of calibrating the absorbers was finally solved by using the titration method of Walker, Bray, and Johnston (*12*) to determine the stage of conversion of the hydroxide to carbonate. The ordinary method of double titration with phenolphthalein and methyl orange as indicators did not give the desired precision for this analysis on account of the high dilution of the alkali. The following procedure gave excellent satisfaction:

A titration vessel was provided with a 3-hole stopper, one hole having a glass plug and the other two having short lengths of glass and rubber tubing. Two drops of 0.5 per cent thymol blue indicator were added to the bottle, the stopper was inserted, and the vessel was flushed out with carbon dioxide-free air. A definite amount of 10 per cent barium chloride solution, 0.01 *N* with respect to barium hydroxide, was pipetted into the titration bottle, which was then weighed before and after introducing the sample, and the excess hydroxide was titrated with 0.01 *N* hydrochloric acid after inserting the tip of the buret through one hole of the rubber stopper. The titration was carried to a definite

end point at about pH 8.8, as compared with a well-buffered borax–boric acid solution.

The method was entirely satisfactory, provided a large excess of soluble barium was present to insure the complete precipitation of carbonate and provided the end point was approached slowly. A titer greater than that of the barium hydroxide added represents hydroxide, while a smaller titer represents bicarbonate. A carefully prepared solution of

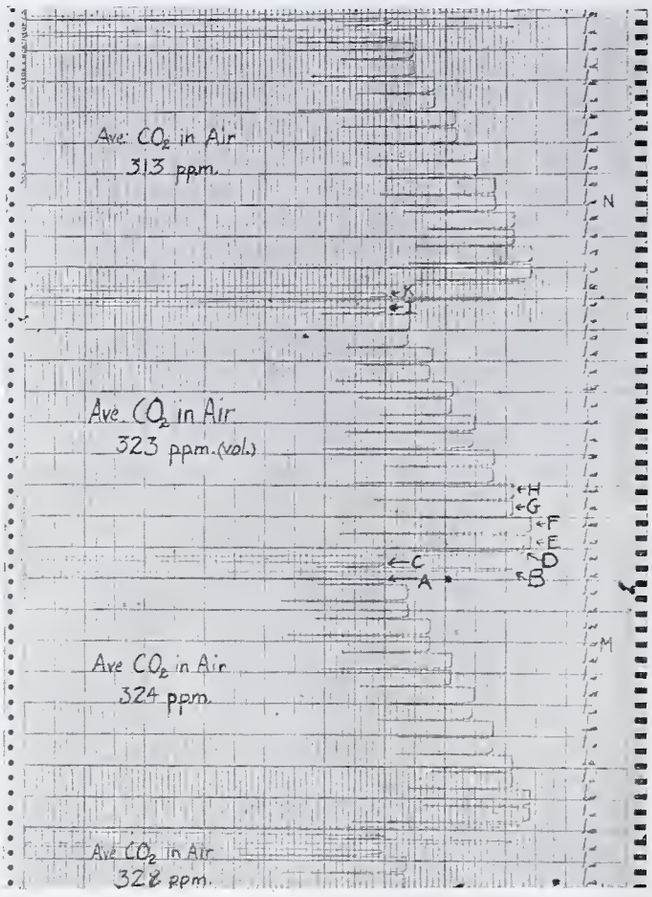

FIGURE 4. SECTION OF RECORDER PAPER, ILLUSTRATING TYPE OF RECORD OBTAINED

Width of paper, 25 cm. (10 in.); paper speed, 20 cm. (8 in.) per hour.

sodium carbonate in carbon dioxide–free water does not change the blank titer.

In carrying out the calibration, about 50 ml. of alkali were introduced into the thermostated absorber and air was aspirated through the solution until the desired amount of hydroxide was converted to carbonate, as indicated by the conductance of the solution. Then carbon dioxide–free air was drawn through the solution until the recorder showed a constant resistance. The solution was withdrawn and titrated as indicated. Typical calibration curves are shown in Figure 2.

Because of the fact that the temperature coefficients of conductance of hydroxide and carbonate differ appreciably, calibration must be made for each temperature at which it is desired to operate. The temperature compensation coil of the recorder employed was designed for dilute sulfuric acid. Dilute sodium hydroxide has nearly the same temperature coefficient as the acid and therefore the calibration curves at different temperatures converge at the hydroxide end. As the temperature coefficient of the carbonate is considerably greater than that of the hydroxide, the calibration curves become steeper at higher temperatures. Accordingly, the instrument may be expected to show a greater change of conductance for a given amount of absorption the lower the temperature of the solution. It will be noted that the response of the recorder to the conversion of hydroxide to carbonate is linear over a wide range.

CARBON DIOXIDE AUTOMETER

The conversion of the laboratory model of the sulfur dioxide autometer (*9*) into a carbon dioxide autometer was completed when a method was devised for drawing a definite small volume of air (for example, 300 cc. per minute) through absorbers of type 2 (Figure 1), which could readily be mounted in place of the sulfur dioxide absorbers. Since the air stream was aspirated through one absorber for 2 minutes before changing to the other, it was necessary to supply a sample of 600 cc. for each aspiration. The flowmeters on the sulfur dioxide machine were discarded and a steel gas meter was constructed, by means of which an exact volume of air could be delivered for each aspiration. A section of this meter is shown in Figure 3, which is a diagram of the air-flow control system. The meter consists of 2 flat chambers connected by a U-tube and mounted on a pivot. Each chamber communicated through glass and rubber tubing to an absorber and also through a valve (*H* or *I*) to the source of the sample. Enough mercury was added to fill one chamber and the U-tube. Air volumes smaller than 600 cc. could be obtained by using more mercury. The two valves leading to the gas meter were operated by the same cam lifters which operated the valves used for shifting the air stream from one absorber to the other, so that air was permitted to enter one chamber of the gas meter from the outside source, while the air in the other chamber was being aspirated through the absorber. In Figure 3, valves *G* and *H* were open, while valves *I* and *K* were closed, and vice versa. Electrical contacts were provided on each side of the gas meter so that when a chamber was completely filled with mercury, the fact was recorded on the chart with the conductance record. The gas chambers were made as flat as possible, and also allowed to move on the pivot, in order to minimize the effect of the changing hydrostatic head of the mercury on the rate of flow of the gas through the absorber.

The suction was adjusted by means of the needle valves and the 2.5-liter equalizing bottle, so that the full sample from the gas meter was drawn through one absorber a few seconds before the air stream was shifted to the other absorber. The bleeder served to maintain the pressure in the equalizing bottle at a constant reduced value and set a definite limit to the height to which the mercury could be drawn in the tubes above the gas meter. The valves *A* to *F* were used to alternate the source of the sample in order that any slight differences between the two absorbers could be compensated for, as in the case of the sulfur dioxide autometer. In operation, whenever fresh portions of solution were placed in the absorbers, carbon dioxide–free air was drawn through valves *A* and *F*, to each of which was attached a large tube of soda lime. This aspiration adjusted the temperature of the solution and established an accurate zero for the determination. After each absorber had drawn one sample of carbon dioxide–free air, the valves *A* and *F* were closed and valves *B* and *E* opened, until seven aspirations had been completed in each absorber. Then fresh solution was placed in the absorbers, one aspiration each of carbon dioxide–free air given, and valves *C* and *D* opened for seven more aspirations.

A complete cycle was accomplished in 64 minutes, and each solution was aspirated for 16 minutes out of the 32 minutes, during which it remained in the absorber. This arrangement proved to be suitable for long-continued studies of photosynthesis and respiration. For other purposes it might be desirable to employ a cycle of different type or length. On account of the frothing of the solution during aspiration, it was impossible to measure the conductance of the solution at

that time, and the recorder was, therefore, connected while the solution was quiescent.

Figure 4 is a photograph of a section of the recorder paper, illustrating the type of record obtained.

At point *A*, the conductance of the solution in absorber 1 was measured and the solution was discharged, fresh solution being added immediately, which is indicated by point *B*. Points *C* and *D* represent a similar condition for absorber 2. During the latter time period, absorber 1 was being aspirated with carbon dioxide-free air, the result of which is recorded at *E* and the corresponding value for absorber 2 is shown at *F*. *G* and *H* represent the results of the first aspiration in the two absorbers, respectively, with air containing carbon dioxide. This process was continued with six more 2-minute aspirations in each absorber until the absorbing liquid was drained out after the conductivity was finally measured at *I* and *K*. The track *M-N* was drawn by a pen mounted on a relay connected with the electrical contacts on the mercury gas meter. The pen was pulled to the right when each chamber was filled with mercury. The track *M-N* proves that the full gas sample was delivered at each aspiration. The average value of the carbon dioxide concentration during each half-hour period is given on the chart. Fifty milliliters of solution were used in the analyses illustrated in Figure 4. The volume now employed is 40 ml., which causes a correspondingly greater response of the recorder.

The sulfur dioxide autometer was modified slightly in two other respects. The 500-cc. constant-level bottle was eliminated and capillary tubes of less than 1-mm. bore were mounted on the pipets to extend along and above the large supply bottle. The upper ends of these tubes were connected to the top of the bottle and provided with an outlet through a soda lime guard tube. The pipets delivered only 0.3 ml. more solution when the supply bottle was full than when it was nearly empty. The 20-liter bottle held enough solution for 125 hours of operation.

Finally, it was found that the temperature of the autometer chamber could not be controlled closely enough for the carbon dioxide determination, and the absorbers were mounted in a small water bath thermostatically controlled to about 0.01° C. The thermostat was 10 × 25 × 25 cm. and provided with a glass window in front and glass tubes soldered through the bottom for draining the absorbers.

Table III. Hourly Differences between Two Absorbers Sampling from Same Air Stream

(Average hourly concentrations calculated by same method as that used for calculating absorption data)

Date 1933	Number of Hours Averaged	Average Concentration CO_2 in Air	Hourly Difference between Absorbers Maximum	Average
		P. p. m.	%	%
Jan. 19, 20	22	322 ± 3.5[a]	1.8	0.45
Jan. 25, 26	23	325 ± 9.4	1.1	0.42
Jan. 27, 28	23	323 ± 3.3	1.7	0.44
Feb. 2, 3	17	337 ± 7.8	0.8	0.32
Feb. 10	12	336 ± 16.5	1.2	0.46
Feb. 11–13	38	301 ± 10.9	1.2	0.44

[a] Standard deviation.

Precision of Absorption Data

During the autumn of 1932 an extended observation was made of the carbon dioxide exchange of alfalfa growing under natural conditions. This experiment will be described in detail in another paper. In order to obtain a definite idea as to the error involved in the gas-exchange measurement, the autometer was operated during the following winter while the ground was covered with snow. Both absorbers drew air through the same intake tube. The machine was located near an open field 5 miles from Salt Lake City and there was little possibility of its being influenced by smoke from a few widely scattered farm homes in the neighborhood. The data were treated in a manner similar to that used in calculating the absorption data. The value of the carbon dioxide concentration indicated by absorber 1 during one half-hour period was averaged with the analysis from absorber 2 during the next half-hour period. Similarly, the analysis from absorber 2 in the first period was averaged with that from 1 in the second period. This method of calculation was necessitated by the fact that the machine alternated the source of the sample with each absorption period. Table III gives the average and maximum differences between the two absorbers from 135 hourly determinations taken at random. The average difference was less than 0.5 per cent in each group of analyses, and exceeded 1.0 per cent in only 10 per cent of the cases. It may be possible in the future to attain higher precision than this, because, while the uncertainty of reading the recorder was about 0.1 scale division, corresponding to about 1 p. p. m. of carbon dioxide or about 0.3 per cent of 300 p. p. m., in practice the concentrations were calculated from both the six and the seven carbon dioxide aspirations in each series, and these values were then averaged, thus reducing the error of calculation. It is of course probable that at least some of the differences were due to occasional peaks of concentration of short duration which affected one absorber more than the other. It is interesting to note from Table III that the carbon dioxide of the atmosphere varied appreciably from day to day as well as during the day.

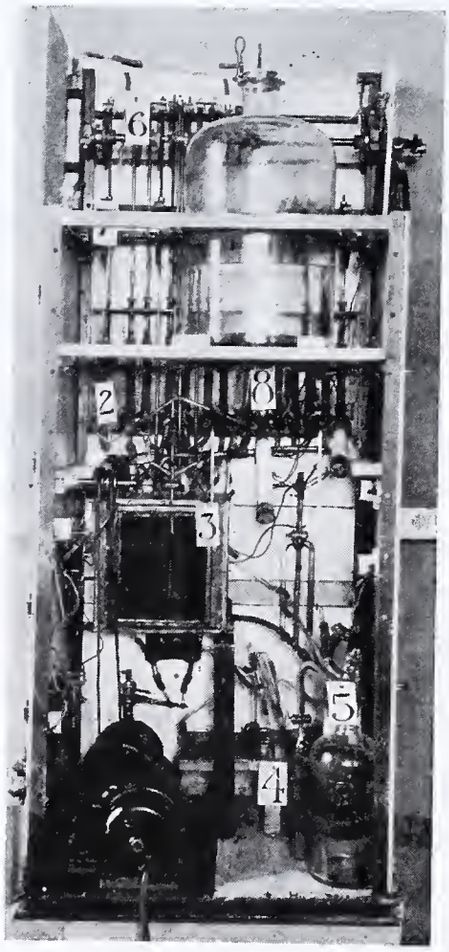

Figure 5. Completed Assembly

1, Supply bottle. 2, Pipets. 3, Absorbers and thermostat. 4, Mercury gas meter. 5, Equalizing bottle. 6 and 7, Cam systems. 8, Automatic valves.

Simplified Apparatus

For long-continued observations of carbon dioxide absorption or evolution, automatic apparatus is practically indispensable on account of the time and labor which would be necessary to obtain the information without the autometer. However, if only a limited number of observations are required, a simplified hand-operated apparatus might be desir-

able. Several assemblies of such apparatus have been constructed. Absorbers of type 2, Figure 1, were employed. The simplest method of drawing and measuring the air sample was by means of a large aspirator bottle, but the sample was most conveniently drawn through an extra valve on the equalizing bottle of the autometer, thus making use of the electrically operated suction pump. A water pump or a

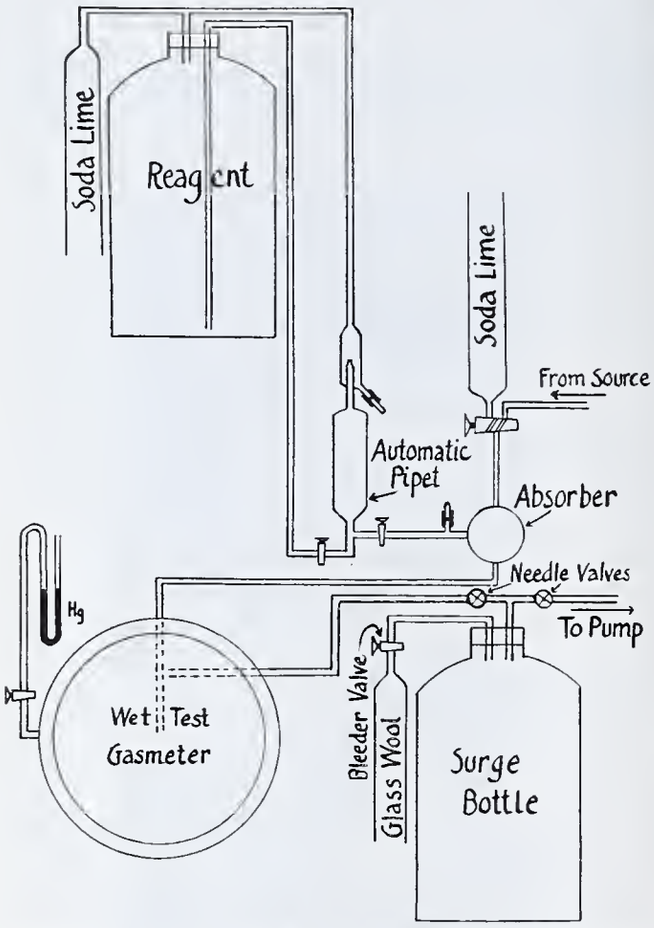

FIGURE 6. DIAGRAM OF HAND-OPERATED APPARATUS FOR DETERMINING CARBON DIOXIDE IN AIR

connection to the intake manifold of an automobile engine gave good results also. The gas was then measured in a wet-test gas meter inserted between the absorber and the suction control apparatus. In the early work, a capillary flowmeter was used instead of the gas meter, but it did not appear to offer the precision necessary for the purpose in hand. The flowmeter would be useful for less precise work. A diagram of a satisfactory assembly is shown in Figure 6. Difficulty was encountered in measuring the air volume accurately in the gas meter on account of the resistance of the absorber. This difficulty was overcome by attaching a three-way stopcock to the intake so that the air stream could be adjusted with carbon dioxide-free air before the sample to be analyzed was started. At the end of the analysis carbon dioxide-free air was aspirated again. The gas meter was read each time the three-way stopcock was turned.

A number of analyses were made by the above procedure using 0.1 *N* sodium hydroxide. The excess alkali was titrated with 0.025 *N* hydrochloric acid by the method of Walker, Bray, and Johnston (*12*) already discussed. The autometer was operated simultaneously, both sets of apparatus sampling from the same source. Each experiment was continued for 60 to 90 minutes. The average values of the carbon dioxide given by the two methods are summarized in Table IV. The maximum difference of 0.7 per cent between the two independent analyses indicates a satisfactory evaluation of concentration of the gas in air. The high carbon dioxide concentrations noted in Tables I and IV were observed in the air of the laboratory. The normal values represent for the most part samples taken from outside.

TABLE IV. CARBON DIOXIDE IN SAME AIR STREAM AS DETERMINED BY TITRATION AND BY AUTOMETER

Source	Duration of Sampling	Average Carbon Dioxide Titration	Autometer	Difference
	Min.	*P. p. m.*	*P. p. m.*	%
Outside	90	333	332	0.3
Outside	90	326	326	0.0
Outside	90	332	333	−0.3
Outside	90	330	328	0.6
Room	60	705	710[a]	−0.7

[a] CO_2 varied from 600 to 850 p. p. m.

A hand-operated apparatus of the type described would doubtless give very satisfactory absorption data if it were provided with two absorbers sampling simultaneously. The concentration of the alkali solution could be measured either by titration, as indicated above, or by conductivity. If the latter method were chosen it would probably be advantageous to have at least two pairs of absorbers with different cell constants so that different concentrations of alkali could be employed. The analyses could thus be completed in a few minutes or extended for several hours, as desired. It would also be necessary to thermostat the apparatus accurately for conductivity measurements.

SUMMARY

Automatic apparatus has been constructed for the continuous determination of atmospheric carbon dioxide from two sources of supply. For example, the machine can draw its air from intake and outlet of an experimental chamber, thus making possible the evaluation of the carbon dioxide exchange in an air stream passing through the chamber. The maximum error of the total concentration of the gas in the air is shown to be less than 1 per cent and the average error of the difference between the two sources of supply is less than 0.5 per cent.

The apparatus employs an absorber capable of removing all the carbon dioxide from an air stream of 350 cc. per minute by means of 40 cc. of 0.005 *N* sodium hydroxide. The essential features of this absorber include a fritted Pyrex glass disk to divide the air stream into fine bubbles and a small amount of normal butyl alcohol to depress the surface tension of the liquid, thus increasing the persistency of the bubbles. The apparatus also utilizes a special mercury gas meter for dispensing the air sample accurately.

Finally a simplified hand-operated apparatus is described.

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A Durable Glass Electrode

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THE glass electrode of the novel form shown by AB in Figure 1 has been found convenient for use in pH determinations, and is no more fragile than any other instrument made of glass. It has the form of a spiral condenser, the spiral of which is made of special (Corning 015) glass. For the electrodes now in use the spiral, which has fourteen turns of about 2.5 cm. diameter, is made of 92 cm. of the commercial tubing, with an external diameter of 5 mm. and walls about 0.6 mm. thick. The precise dimensions are not important. The rest of the apparatus AB is made of Jena thermometer glass, the spiral being joined to the inlet tube A and the outlet tube B at the points a and b, with Corning seal glass H. The arm L is fitted to hold a silver-silver chloride electrode, P', and the space between the jacket J and the spiral is filled with 0.1 N hydrochloric acid. (Any solution having a definite pH and chloride ion concentration may be used.) The solution, the pH of which is to be measured, is placed inside the spiral, which has a volume of about 7 cc., and is connected through a liquid junction with saturated potassium chloride at the point K with a reference calomel electrode.[1]

In connection with their study of this electrode the authors have developed a convenient method for making the liquid junction between the solution the pH of which is to be measured and saturated potassium chloride solution. The operation of the device is as follows: With the stopcock S closed the solution is poured into the upper portion of the vessel AB. The stopcock is then placed in position to connect the tube B and the reject tube T, but is turned clockwise before the solution has passed point a. Rotating the stopcock further in the same direction connects the tubes K and T and also permits the flow of saturated potassium chloride from the reservoir R through the extra bore g in the rear end of the stopcock and out through the reject tube T. This flow will be clear from a study of the plan of the apparatus in the lower part of Figure 1. Another clockwise turn of the stopcock through 120° forms a liquid junction at the point e between the solution in AB and the saturated potassium chloride solution, the latter being in electrical connection with the saturated calomel electrode P. (E. Machlett and Son, 50 William St., Long Island City, N. Y., are prepared to make the apparatus as shown in Figure 1.)

Although the glass used in the spiral has six hundred times the thickness of that used in the membrane type of glass electrodes described by MacInnes and Dole (*5*) and MacInnes and Belcher (*4*), the area exposed to the solution is greater by approximately that factor, so that the (apparent direct current) resistance is approximately the same as that of one of the thinner membrane electrodes. Seventeen spiral electrodes made as described had resistances ranging from 19 to 30 megohms with an average of 25 megohms. The "asymmetry-potentials"—*i. e.*, the more or less permanent potentials existing in the glass—are, however, much greater than those observed with the membrane electrodes. For the latter they are usually of the order of one or two millivolts. With the spiral type electrodes their initial values are as high as 100 mv. However, if the electrodes are kept filled with water these asymmetry potentials slowly decrease. For instance, one electrode showed a decrease of asymmetry potential of 8 mv. the first day. This rate of change steadily decreased until after a month the asymmetry potential showed no further change. The variations observed are always in the direction of a decrease of the asymmetry potential. In practice the sum of the asymmetry potential and that of the reference electrode, which we will call E_0', can be obtained by a measurement involving a convenient buffer solution whose pH value is accurately known. The relation between the measured potential E, the pH value, and E_0' is, of course, given by the usual equation

$$\text{pH} = \frac{E - E_0'}{2.303\, RT/F} \qquad (1)$$

That comparatively thick glass can be used for glass electrodes if the surface is also increased in proportion to the thickness has recently been shown in an interesting paper by Thompson (*8*). This worker has studied electrodes of test-tube shape, with a metal coating, to which contact is made, on the exterior surface. With such electrodes the potential which corresponds to E_0' as defined above is, however, subject to small but unpredictable changes, probably due to replacing a reversible electrode, such as the silver-silver chloride electrode P', by a glass-metal contact at which, so far as we know, no definite electrochemical reaction takes place.

Measurements, using the spiral type of electrode, on a series of solutions covering a wide range of pH values are given in Table I. The pH value of the potassium acid phthalate buffer was used to obtain the value of E_0' of Equation 1, and the other measured values given in the third

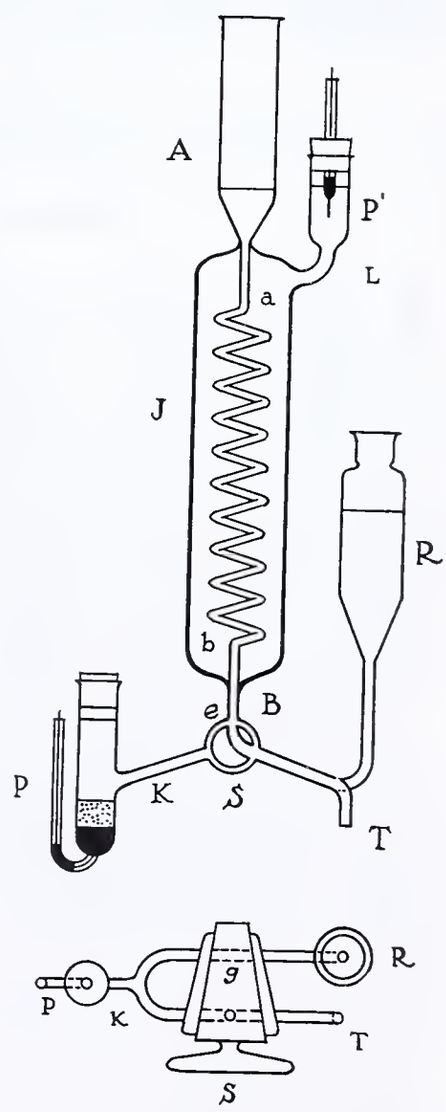

Figure 1. Diagram of Glass Electrode

[1] A variant of this design which has been found useful in certain cases is to have the external surface of the spiral bathed with the solution the pH of which is to be determined. It appears desirable to have the active surface of glass completely immersed, on account of an effect, described by Kahler and De Eds (*3*), on the measured potential, due to a film of solution on an exposed surface.

column of the table are computed from the measured potentials. The two figures for the pH of each solution indicate the reproducibility obtained on refilling the spiral. It will be seen that there is agreement within about 0.01 pH unit between these measured values and the published "accepted" values given in column 4 within the pH range 1 to 8. Above the latter value, however, there is the familiar deviation of the glass electrode. The accepted values are all on the basis that the potential of the tenth normal calomel electrode is 0.3376. The value for the pH of 0.1 *N* hydrochloric acid is from Clark (*1*), that of the phthalate buffer from work of the authors (*4*), and the pH values of the diethylbarbituric acid buffers from Michaelis (*6*). The pH of the 0.01168 *N* hydrochloric acid has been found by interpolating a value of the activity coefficient from the values given by Scatchard (*7*). It seems probable that within the range in which the glass electrode is effective the new measured values are as accurate as the published ones.

The potential measurements recorded in Table I were obtained in a constant-temperature room at 25° ± 0.1° with the potentiometer and Compton electrometer described by MacInnes and Belcher (*4*). In addition many routine measurements have been made in this laboratory on biological solutions using for the potential determinations the vacuum tube apparatus described by Hill (*2*).

With both these potential-measuring equipments insulation and electrostatic screening have been carefully studied. Although the authors do not suggest any relaxation of care with respect to these factors, their importance is not as great as it sometimes is in work of this kind, because the glass electrodes described in this article have comparatively low resistances.

Table I. Comparison of Accepted and Measured pH Values of Buffer Solutions

Solution	Measured E. M. F.	pH Value Measured	pH Value Accepted
0.10 *N* Hydrochloric acid	−0.1360 −0.1362	1.06 1.06	1.06
0.01168 *N* Hydrochloric acid	−0.0807 −0.0812	1.99 1.99	1.98
0.05 *N* Potassium acid phthalate	0.0370 0.0367	(3.98)	3.98
Diethylbarbiturate buffer	0.2143 0.2137	6.98 6.98	7.00
Diethylbarbiturate buffer	0.2753 0.2743	8.01 8.00	8.00
Diethylbarbiturate buffer	0.3297 0.3289	8.93 8.92	9.00
Diethylbarbiturate buffer	0.3601 0.3614	9.44 9.45	9.60

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Estimation of Dextrin in the Presence of Glue

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Admixture of dextrin powder with glue may be readily detected by microscopic examination, using mineral oil or some high-boiling alcohol as a mounting medium. However, if the dextrin has been dissolved in the glue liquor prior to drying the glue, the addition is not so obvious. Some dextrins will not respond to the iodine test, especially if the glue is highly colored; but any dextrin may with certainty be detected by hydrolyzing the mixed glue with dilute hydrochloric acid and then testing the liquid for dextrose with Fehling's or Benedict's qualitative solution. The protective colloid action of the protein and its hydrolysis products tends to make the copper oxide precipitate so fine that it appears yellow, and if all the copper is not reduced, the solution may appear to be green.

For the precise estimation of dextrin in glue, the following method proved satisfactory:

Soften 0.6 gram of the glue under test by soaking in 10 cc. of dilute hydrochloric acid (5 parts of concentrated hydrochloric acid to 100 parts of water). Hydrolyze the mixture slowly at low temperature (overnight at about 60° C.). After neutralization make up the solution to exactly 50 cc., and determine the dextrose content by Benedict's quantitative method.

Benedict's Quantitative Solution (*2*). Dissolve 200 grams of sodium citrate, 200 grams of sodium carbonate, crystallized (equivalent to 75 grams of anhydrous sodium carbonate), and 125 grams of potassium thiocyanate (sulfocyanide) in enough hot distilled water to make up to about 800 cc. Dissolve separately 18 grams of purest copper sulfate crystals (air dried) in about 100 cc. of distilled water, and pour into the first solution with constant stirring. Add 5 cc. of a 5 per cent solution of potassium ferrocyanide, and then make up to 1000 cc. with distilled water. The solution is stable, and 25 cc. are reduced by 0.05 gram of dextrose.

To make the analysis, a 150-cc. flask is held in a stand over a Bunsen burner, at such a height that the reagent solution can be kept briskly boiling by a small flame. In this flask are placed 3 to 4 grams of anhydrous sodium carbonate and 25 cc. of the reagent, the mixture being heated until most of the carbonate is in solution. The glue solution is now run in slowly, until a chalk-white precipitate is formed and the blue color lessens perceptibly in intensity. The glue solution is now run in still more cautiously, with constant boiling, until disappearance of the last trace of blue indicates the end point. If less than 5 cc. of glue solution has been used, the solution is accurately diluted so that about 10 cc. will be necessary, and the titration repeated with this diluted solution. Should the mixture in the flask become too thick, boiled distilled water may be added to replace that lost by evaporation.

In using this method, no trace of reduction was shown by a glue known to be pure, which was run as a check or blank in the quantitative test, after having been proved free from reducing substances by qualitative test. Mixtures of this glue with several commercial dextrins gave concordant results. In converting the dextrose figure to dextrin, it should be remembered that commercial dextrins contain variable percentages of water, dextrose, etc. The dextrose figure multiplied by the factor 0.9 gives a close approximation to the amount of dextrin present (*1*).

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Quantitative Separation of Small Amounts of Zinc from Material Rich in Iron

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IN TECHNICAL analyses zinc is usually determined by the volumetric ferrocyanide method in which the iron is separated by precipitation with ammonium hydroxide, and the manganese by the addition of bromine or ammonium persulfate to the ammoniacal solution. This method is rapid and accurate in skilled hands. However, the separation of iron and manganese from zinc is open to criticism, because of the retention of zinc in the iron and manganese precipitates.

When dealing with the usual ores and metallurgical products, this difficulty is overcome by dissolving the washed precipitate in hydrochloric acid and repeating the precipitation, and by adding ammonium chloride to the solution before each precipitation of iron with ammonium hydroxide (*3*, *4*). If only a few tenths of a per cent of zinc are to be separated from a relatively large amount of iron, the above method of separation is not satisfactory.

Precipitation of zinc as zinc sulfide from a solution made slightly acid with sulfuric or formic acid (*2*) gives a good separation of zinc from iron and manganese when dealing with ordinary ores. It is difficult, however, to obtain the careful adjustment of acidity necessary when minute amounts of zinc are to be separated from large amounts of iron. The following method has been developed to overcome these objections:

PROCEDURE. Weigh 5 grams of material into a 400-cc. beaker and decompose with hydrochloric acid, with the addition of nitric acid if sulfides are present. After decomposition, evaporate to dryness and bake. Cool, add about 10 cc. of hydrochloric acid, and warm gently until all soluble matter is dissolved. Filter, and wash the insoluble material free from chlorides. Neutralize the excess hydrochloric acid with ammonium hydroxide, leaving the solution sufficiently acid to prevent hydrolysis of the iron. Add an excess of a sodium citrate solution, prepared by dissolving 1 pound (453.6 grams) of sodium citrate and 20 grams of citric acid in sufficient water to make one liter of solution. It is not possible to state the exact quantity of sodium citrate which will meet all conditions, as this depends upon the amount of iron, and on the excess hydrochloric acid present. In general from 20 to 50 cc. of the solution are required. There should be enough hydrochloric acid to prevent the formation of any precipitate upon the addition of the sodium citrate solution, and enough sodium citrate solution to react with the excess hydrochloric acid.

Dilute to 250 to 300 cc. and pass hydrogen sulfide through the cold solution until it is thoroughly saturated and the precipitate coagulates. Filter and dissolve the precipitate with hot dilute nitric acid into the beaker used for the precipitation. Evaporate to dryness and bake. Cool, dissolve the residue in hydrochloric acid, add about 6 grams of ammonium chloride, and proceed by any of the usual methods for the determination of zinc.

A small amount of iron or manganese, in case of a manganese ore, will accompany the sulfide precipitate and may be separated by the usual methods. The amount is so small as to cause no serious difficulty. Lead and copper are precipitated quantitatively with the zinc. This separation may be found useful for the determination of lead and copper in low-grade products, such as mill tailings.

Nickel is not precipitated from a cold solution, and from a warm solution the precipitation is slow. This method was used for the separation of nickel and zinc by Crookes (*1*), who passed hydrogen sulfide through the cold solution, and stated that a small amount of nickel may be precipitated by long treatment with hydrogen sulfide.

Cobalt is precipitated. A single experiment on material free from nickel and low in cobalt gave a quantitative separation. When tried on material carrying about 5 per cent each of cobalt and nickel, it was not so successful. The cobalt precipitated slowly and required long treatment with hydrogen sulfide to complete the precipitation. As a result of this long treatment, some nickel accompanied the cobalt precipitate, which seems to verify the statement of Crookes, mentioned above.

To test the accuracy of the separation the following work was done:

Five grams of Bureau of Standards Crescent iron ore, containing 58.6 per cent of iron, were treated as described. To the filtrate from the insoluble material was added 0.0161 gram of C. P. zinc, dissolved in dilute hydrochloric acid. After completing the separation as outlined, 0.0160 gram of zinc was recovered.

Five grams of a manganese concentrate, containing about 44 per cent of manganese, were treated as described, and to the filtrate from the insoluble material 0.0145 gram of zinc was added. After completing the separation, 0.0140 gram of zinc was recovered.

A flotation tailing, low in zinc and carrying approximately 35 per cent of iron, gave the following results by this method: 0.25, 0.25, 0.25, 0.24, 0.26, 0.26, and 0.26 per cent of zinc.

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Air Pressure for Blast Lamps

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THE amateur glass blower, who has no means of obtaining an air-pressure pump and tank, may improvise an efficient substitute from a second-hand vacuum sweeper. By dismantling the unnecessary accessories and removing the dust plate, a very compact apparatus results, which may easily be stored in a table drawer, to allow more working room. By using a large rubber stopper, in which a Y-tube is inserted, in the manifold where the dust bag is ordinarily clamped, three blast lamps can be easily supported, and even four, if necessary. If an oxygen generator is set up and fed into the intake, the flame produced is very suitable for working Pyrex glass.

This apparatus may be used for igniting crucibles or for any other work where air pressure is requisite. It should be as easy to improvise as the Muencke blower of Robey (*1*) and perhaps more convenient to use. A rheostat in series with the motor and the original snap switch fastened firmly to the bench are useful accessories.

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RECEIVED March 24, 1933.

"Oxidizing Agent" and Peroxide in an Otto Cycle Engine Cylinder

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A description is given of the apparatus used and the results obtained in experiments on sampling the cylinder contents of a Ricardo E. 35 engine, from different parts of the compression space and at different times during the compression, exhaust, and inlet strokes. Using a slightly acid solution of potassium iodide, quantitative estimations were made of an "oxidizing agent" which was assumed to indicate a definite stage in the progress of combustion of the three fuels used (benzole, a straight-run spirit, and an ethyl gasoline).

Mention is made of two theories of combustion and fuel-knock in an engine, and their relation to the research reported is discussed.

SINCE the early part of the nineteenth century chemists have been interested in the mechanism of the combustion of hydrocarbons and a great volume of work has been done, in general either on slow combustion utilizing sealed vessels or a steady flow of gas through heated tubes, or on explosions in a bomb. Since the advent of prime movers operating on the Otto cycle and using hydrocarbons as fuel, the problem has assumed more than an academic interest and is now of primary importance to the engineer.

During each of the four stages of the Otto cycle (suction, compression, explosion and expansion, and exhaust) chemical changes take place in the cylinder contents and in an engine the complete cycle is repeated continuously with great rapidity. At first sight the time element might be assumed to complicate the problem of determining, for a single cycle, the intermediate products between a hydrocarbon-air mixture and its products of combustion, but the continued repetition enables a small sample to be withdrawn each cycle at the same instant and this procedure can be continued until sufficient gas has been collected to perform a chemical analysis. Slow combustion and bomb experiments can at best only serve as guides in the more practical problems encountered in work on an engine delivering power.

This paper describes experiments performed on the Ricardo E. 35 variable compression engine at Cambridge University. Although the investigation was not carried as far as could be wished, the results reported seem worthy of being placed on record as an indication of the possibilities of this type of investigation. With the engine delivering power, a small sample of the cylinder contents was abstracted once each engine cycle from a part of the compression space and at a point in the cycle, both of which could be predetermined. When sufficient gas had been collected from the cylinder, a chemical analysis was performed and (in the latter stages of the work) quantitative estimations were made of an "oxidizing agent." The experiments were suggested by the University Research Panel of the Aeronautical Research Committee as the logical outcome of others described in an Aeronautical Research Committee publication (*4*). Samples had been taken from the exhaust pipe of an E. 35 engine while it was rotated by motor (ignition switched off and a high jacket temperature maintained), aldehydes and peroxides had been detected, and it seemed advisable to perform similar experiments on an engine delivering power, the samples being taken from the cylinder.

Sampling Valve

From seat to gas outlet the valve (Figure 1) measured a little over 6 inches (15 cm.) and water cooling was provided for a length of 5 inches (12.7 cm.) from the seat. The cooling arrangement was suggested by G. F. C. Gordon, of the Cambridge University Engineering Department, and consisted of a double spiral square thread forming two independent spaces, water traveling through one space to the seat and returning through the other. This cooling served the double purpose of keeping the valve intact when exposed to heat in the engine cylinder (the method of construction involved brazing at the tip) and of chilling the sample after passing the seat. The valve was threaded on the outside for 4.75 inches (12 cm.) from the tip and screwed into one of the four standard spark-plug holes in the engine cylinder: when the desired position had been reached the valve was locked by a locking collar, the extreme position being with the valve seat at the center of the cylinder. Difficulties were encountered in making the valve gas-tight: no satisfactory method of lubricating the stem could be devised, carbon and rust were deposited while sampling was in progress, and in consequence it was impossible to guide the valve stem for at least 6 inches (15 cm.) from the seat. They were overcome by turning the valve stem from a rod of tool steel and providing it with a hemispherical head (seating into a very narrow mild steel seat) and a guide formed by a cast-iron piston screwed to the other end of the stem. The piston was lubricated by three screw-down grease cups spaced at 120° intervals round the sampling valve and beyond it a rod, screwed both to the end of the valve stem and to an adjustable collar terminating in a case-hardened hemispherical head, completed the moving part of the valve.

Sampling Mechanism

The valve and the actuating mechanism were fixed to plates united by a complicated system of stays in three dimensions and secured to the engine (Figure 2). Motion was transmitted to the valve stem through a case-hardened cone fixed by setscrew to a rod. This rod was provided with two guides and given a reciprocating motion by the engine camshaft through a clutch, a variable timing device incorporated with a wheel carrying the crank pin, and a connecting rod. The angle of the cone was chosen to make its surface perpendicular to the valve at the striking point, so that the thrust should be approximately along the line of valve travel. Any side thrust was taken up by a brass ball (through which the end of the valve projected) held between the fixed plate carrying the reciprocating rod and a small adjustable plate held in position by three setscrews.

As first assembled the arrangement gave a valve opening of 40° (crank angle), but by employing a 5-inch (12.7-cm.) diameter wheel on which was cast a suitable lead balance weight, and a connecting rod of Duralumin (supplied by Messrs. James Booth and Company of Birmingham, Eng-

land), the time of opening was reduced to about 20°. This estimate was arrived at as follows: With the variable timing device in a fixed position and the clutch engaged, the engine was rotated by hand until the cone came into contact with the end of the valve; 50° (crank angle) later contact ceased, but gas did not escape from the cylinder during the whole of this period. Again with the clutch engaged, rotation was continued beyond the point of initial contact of cone and valve; then the clutch was disengaged without disturbing the valve-actuating mechanism, the engine rotated by motor, and the gas outlet from the valve tested for leakage. In this way it was found that gas emerged from the engine cylinder during the 20° to 40° interval of the 50° contact of cone and valve, so that the position of mean opening of the valve (Figures 4 to 6) was taken as 20° earlier than the crank angle at which contact between it and the cone ceased. For any test it was sufficient to determine this "mean opening" for but one setting of the variable timing device, which was graduated in degrees of camshaft angle.

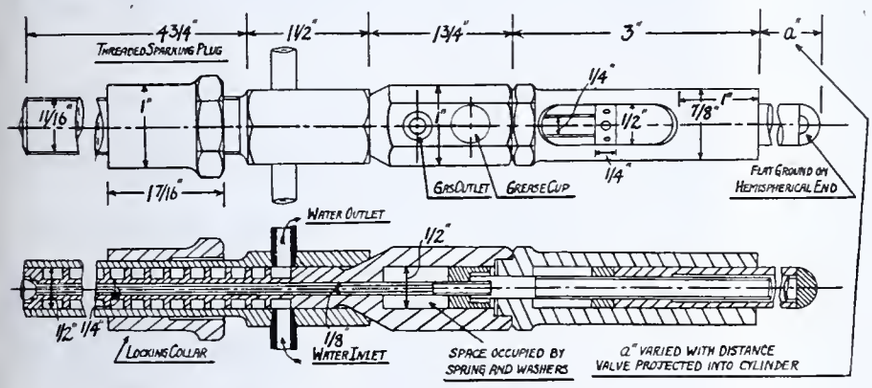

Figure 1. Sampling Valve

The apparatus went into operation early in 1929 and was then believed to be unique in enabling samples to be taken both at different times during the cycle and from different parts of the compression space. Not until September, 1930, (*12*) did the literature consulted contain reference to a valve with similar scope, though accounts of sampling devices fixed in position in the cylinder are to be found prior to 1929.

Qualitative Tests

A pressure-tube connection was made between the gas outlet from the sampling valve and one leg of a T-piece, the two remaining legs being also provided with pressure-tube connections. One of these led to the atmosphere and was fitted with a screw pinchcock, the other led to the sampling apparatus, and by partly closing the outlet to the atmosphere a regulated flow of gas from the engine cylinder was maintained through the sampling apparatus. This consisted of a glass spiral ending in a bulb provided with a drain tap (the whole immersed in a freezing mixture) followed by a series of Arnold bulbs containing selected reagents.

Table I. Qualitative Tests, Compression Stroke

(Fuel, Shell straight-run spirit; compression ratio, 4.5/1; speed, 1100–1150 r. p. m.; jacket water temperature, 60° C.; power, maximum possible; fuel-knock, occasional slight. Mixture fired by two spark plugs diametrically opposite, sampling valve half way to the center of the cylinder on a perpendicular diameter. One inlet valve operated with reduced lift, eventually cut out completely, to avoid contact with sampling valve.)

Reagent	To Detect	Detected
Schiff's	Aldehydes	Yes
Titanic sulfate solution	Peroxides	No trace
Acid potassium iodide solution	"Oxidizing agent"	Yes
Lime water	Carbon dioxide	Yes
Palladium chloride solution	Carbon monoxide	No

Samples were taken at various points during the compression stroke, the results and relevant data appearing in Table I. No trace of peroxide was detected, and in what follows the substance present in the engine cylinder which possessed the property of liberating iodine from a slightly acid solution of potassium iodide is referred to as "oxidizing agent."

Quantitative Tests, Compression Stroke

The method of sampling finally employed was developed as a result of observations on the type of reaction taking place between gas from the cylinder and the potassium iodide solution. This reaction was slow and appeared to be complete in about 3 hours, so that it seemed advisable to arrange for the gas to pass directly from the engine to the test solution and remain in contact with it until the reaction ceased.

Two sets of five gas-sampling tubes (*A* to *E* and 1 to 5) were used, each tube being carefully calibrated and a mark made on a strip of paper pasted on the side. When gas was passed in to the mark the *A* to *E* set contained gas and 50 cc. of test solution, and the 1 to 5 set gas and 25 cc., this being done to simplify the control correction. (Approximately 200 cc. of gas were collected in each tube of the *A* to *E* set, and 100 cc. in each of the 1 to 5 set.) Sampling procedure is illustrated by Figure 3. The vessel *V* was filled with test solution and with *A*, *B*, *X*, and *Y* open it was raised until the level of the solution in the sampling tube *S* was at *A*. *X* was first partly closed (gas was forced into *S*, displacing the potassium iodide solution), then opened again and the level of solution in *S* allowed to return to *A*. This insured that the connection between *A* and *X* contained nothing but gas from the cylinder. To obtain the sample *X* was partly closed, gas passed in until *S* was full, *A* closed, and the clutch on the sampling gear taken out. *A* was then opened, the levels in *S* and *V* adjusted to the mark on *S*, and the sampling tube contained a known volume of gas at atmospheric pressure, in contact with a convenient amount of potassium iodide solution. Throughout the quantitative tests this test solution was standardized at 5 per cent (by weight) and each 300 cc. were acidified by the addition of one drop of strong sulfuric acid.

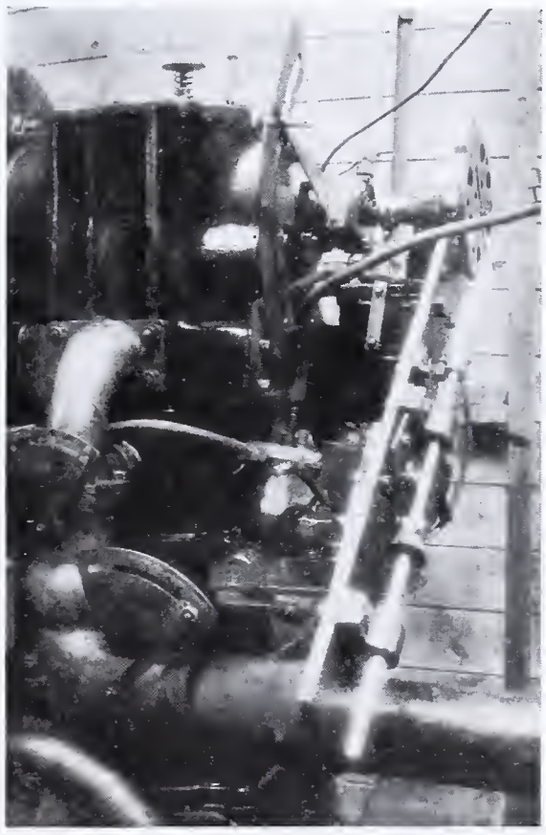

Figure 2. General View of Engine and Sampling Mechanism

The sampling tubes (containing gas and test solution) and a 50-cc. control solution were kept in darkness until the titration was performed (usually about 3 hours after sampling) and during this time the control solution turned slightly yellow. The iodine liberated from all solutions used was titrated by a solution of sodium thiosulfate (starch being added in the final stage to give a more accurate result), part of the same solution being used also to titrate a known amount of standard solution of iodine in potassium iodide. This standard solution (kept in darkness) was made by adding an accurately measured quantity of iodine to a solution of potassium iodide in distilled water, and was used throughout the tests. From the titrations of test, control, and standard solutions, the mass of iodine liberated by the gases from the cylinder was readily calculated and it was taken as a measure of their oxidizing agent concentration by weight. The figures were reduced to 100 cc. of gas and typical results plotted in Figure 4, grams of iodine ($\times 10^{-3}$) against positions of mean opening of the sampling valve in degrees of crank angle. Data not deducible from Figure 4 are given in Table II.

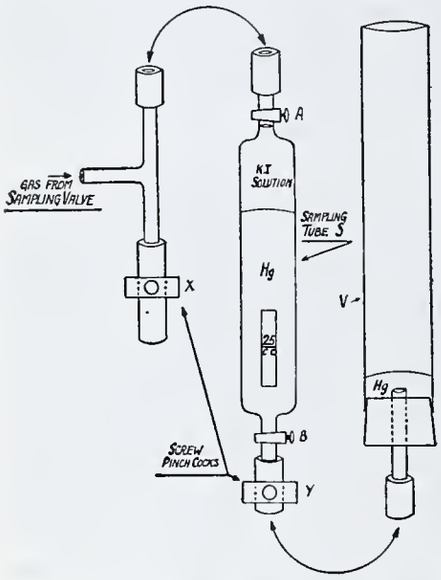

FIGURE 3. SAMPLING APPARATUS

TABLE II. QUANTITATIVE TESTS, COMPRESSION STROKE

(Compression ratio 4.75/1; jacket water temperature, 60° C.; spark advance, 30–35°)

Test	7	10	11	12
Fuel	S[a]	B[b]	B[b]	S[a]
Engine speed (r. p. m.)	1056	1032	1044	1076
Fuel-knock	Occasional slight	None	None	Continuous moderate
Sampling valve position	C[c]	C[c]	A[d]	A[d]
Valve cooling water (° C.)	25	25	18	18

[a] Shell straight-run spirit.
[b] Benzole.
[c] At center of cylinder.
[d] At edge of cylinder.

QUANTITATIVE TESTS, EXHAUST AND INLET STROKES

A 180° rotation of the complete variable timing device on its shaft changed the valve opening from compression to exhaust, and smaller alterations enabled investigations to be made over a wide range of both exhaust and inlet strokes. During these strokes the pressure in the cylinder varies from a value slightly greater than atmospheric to one slightly less, so the sampling technic had to be changed.

The procedure was as follows, 100-cc. capacity sampling tubes being used (Figure 3): The vessel V and the pressure tube connection to S were filled with mercury and Y closed, 25 cc. of potassium iodide solution drawn into S, and A and B closed. The flexible connection was made between V and S; A, B, and Y opened, and S then contained mercury and 25 cc. of superimposed potassium iodide solution.

To sample from the inlet stroke X was gradually closed, the level of the solution in S being preserved by lowering V. When X was completely closed V was lowered still further, drawing the sample from the cylinder until the level of the potassium iodide solution was below the 25-cc. mark on S. A was then closed, V raised until the potassium iodide solution again reached the 25-cc. mark on S, and B closed. When sampling from the exhaust stroke a similar procedure was adopted, but the level of the potassium iodide solution in S was kept above the mark before closing A, in order to obtain the sample at a pressure as close as possible to atmospheric.

The technic gave very consistent results, figures for typical tests being plotted in Figures 5 and 6. Data not deducible from the figures are given in Table III, from which it will be noticed that certain iodine values are omitted from the curves. This was done only when these values were very far removed from the average. A satisfactorily large proportion (80 per cent) of the total number of readings made in the selected tests has been utilized.

TABLE III. QUANTITATIVE TESTS, EXHAUST AND INLET STROKES

(Compression ratio, 4.75/1; jacket water temperature, 60° C.; spark advance, 30–35°. Sampling valve at edge of cylinder, except in test 16 when it was half way to center)

Test	Readings Plotted[a]	Fuel	Engine Speed	Fuel-Knock
			R. p. m.	
1	4	S[b]	1120	Occasional, slight
2	5	S[b]	1086	Occasional, slight
3	4	S[b]	1124	Occasional, slight
4	4	S[b]	1094	Occasional, slight
5	5	S[b]	1100	Occasional, slight
6	5	S[b]	1122	Occasional, slight
8	3	S[b]	1110	Occasional, slight
9	3	B[c]	1096	None
10	3	B[c]	1076	None
12	5	P. E.[d]	1080	None
13	3	P. E.[d]	1074	None
14	4	P. E.[d]	1074	None
16	4	P. E.[d]	1086	None

[a] Five readings were observed in each test.
[b] Shell straight-run spirit.
[c] Benzole.
[d] Pratt's ethyl petrol.

SUPPLEMENTARY TESTS

Gas from the cylinder was either bubbled or drawn directly through titanic sulfate solution at all points during compression, exhaust and inlet strokes (engine delivering power), but no trace of peroxide was anywhere indicated.

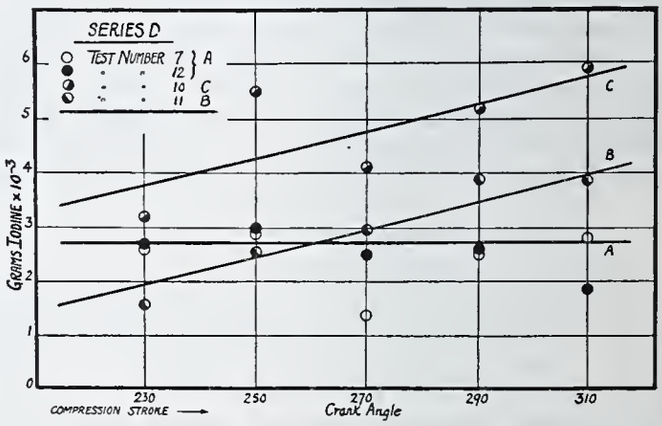

FIGURE 4. COMPRESSION STROKE TESTS

A small pipe was screwed into the inlet manifold and samples extracted from here with the engine delivering power, but neither oxidizing agent nor peroxide was detected.

The engine was allowed to run until the temperature of the jacket cooling water reached 70° C., ignition switched off, and rotation continued by motor. Samples were taken from the cylinder at various points of the cycle while the jacket temperature fell to 50° C., but neither oxidizing agent nor peroxide was detected. (This agrees with a similar experiment described by Callendar, *4*.)

DISCUSSION

OXIDIZING AGENT. In view of the uncertainty concerning the identity of the substance detected and estimated by the liberation of iodine from potassium iodide solution, the term "oxidizing agent" is employed for convenience. The reac-

tion between cylinder contents and test solution, though it commenced immediately contact between the two was established, was slow of completion, and it is known that varying combinations of aldehyde, exhaust gas containing carbon monoxide and carbon dioxide, and air, were abstracted from the cylinder. Naturally the question arises of possible action between air and/or oxides of carbon and aldehyde resulting in the formation of a product capable of liberating iodine from potassium iodide, but reference to Figures 4 to 6 shows (*a*) small quantities of iodine liberated during the compression and late inlet strokes, when the largest proportions of air and the smallest of oxides of carbon are to be expected, and (*b*) small quantities also during the early exhaust stroke when the opposite proportions of air and oxides of carbon are to be expected. This would seem to isolate the oxidizing agent (possibly a nascent aldehyde) as the chief liberator of iodine, and three interrelated assumptions are made, namely, that the appearance of this substance marks a definite stage in the progression of hydrocarbon-air mixture to products of combustion, that liberation of iodine from the slightly acid solution of potassium iodide was proportional to the concentration (by weight) of this substance in the cylinder, and that the same substance was produced at corresponding stages in the combustion of the three fuels used. With these assumptions, the results yield interesting conclusions.

Figures 5 and 6 show that the oxidizing agent concentration increases during the exhaust stroke (1), reaches a maximum early in the inlet stroke (2), and then decreases (3). Combustion of the fuel-air mixture in an engine cylinder is never completed during the power stroke and may therefore be assumed to continue during the exhaust stroke (1). Fresh

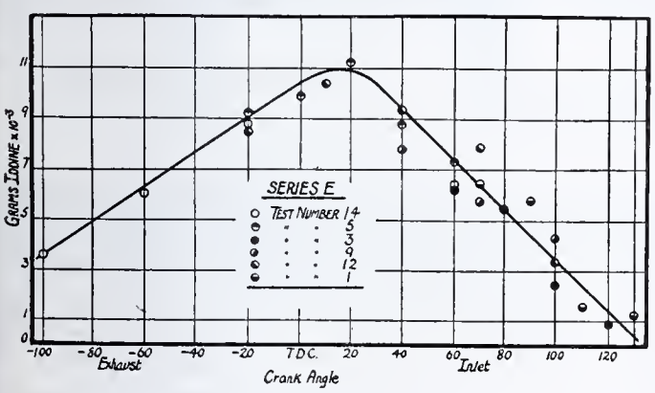

FIGURE 5. EXHAUST AND INLET STROKE TESTS

charge enters the cylinder before top dead center, coming into contact with hot metal surfaces and the hot exhaust gases, and combustion is initiated (2). As the piston moves down on the inlet stroke the continued entry of fresh charge dilutes the mixture in the engine cylinder, accounting for the falling off in oxidizing agent concentration (3). This applies equally well to each of the three fuels used, engine operating with or without fuel-knock.

Figure 4 shows that with the engine running on benzole (a nonknocking fuel) there was a uniform, slight increase in oxidizing agent throughout the compression stroke, and while running on gasoline (with and without fuel-knock) the amount of oxidizing agent remained sensibly constant. Comparison with Figures 5 and 6 shows that the amounts estimated for the end of the inlet and during the compression stroke are approximately the same, and are small compared with those for the early part of the inlet stroke, indicating that oxidation of the fuel-air mixture does not proceed unless contact with hot metal surfaces (and/or exhaust gas) occurs (*10*).

The absence of oxidizing agent in the samples taken from the inlet manifold, and from the cylinder when the engine was motored, can be explained by the considerably lower temperatures at which these samples were obtained.

PEROXIDE. The lack of definite coördination of substance sought with reagent employed in the paper already mentioned (*4*) misled the author into a lengthy search for a true peroxide in the engine cylinder. This matter was discussed in an essay written during the early part of 1930 (*11*) and the point has since been raised by various writers (*1, 2, 3, 9*). Liberation of iodine from potassium iodide solution is not conclusive evidence of the presence of a peroxide, but a reaction with titanic sulfate solution is.

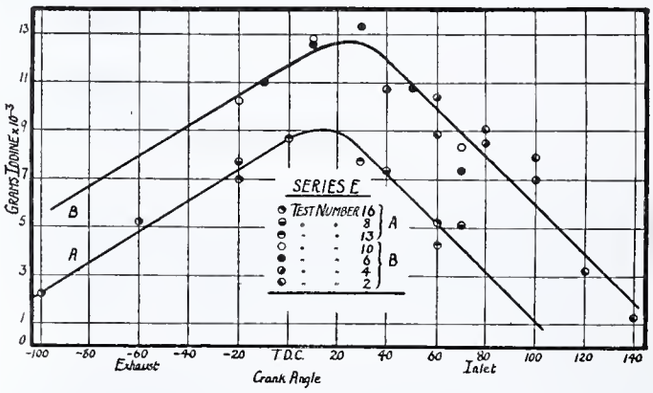

FIGURE 6. EXHAUST AND INLET STROKE TESTS

The experiments reported in this paper show definitely a complete absence of peroxide in the engine cylinder under various combinations of widely differing conditions: (*a*) engine operated on three different fuels; (*b*) engine operated with and without fuel-knock; (*c*) samples taken during compression, exhaust, and inlet strokes; and (*d*) samples taken from different parts of the compression space. They therefore do not support the Callendar "peroxide" theory of combustion and fuel-knock in an engine (*4–8*). If a peroxide be formed during the initial stages of hydrocarbon combustion in an engine cylinder and if this same peroxide be responsible for fuel-knock, it is strange that (whether fuel-knock was present or not) no sign of it could be detected at any point of the cycle from which samples were taken. If a peroxide were formed at all it must have been after the passage of the spark (which is not where the Callendar theory postulates, *5*) and therefore subsequent to the formation of the oxidizing agent herein described.

If it be assumed that the oxidizing agent were an aldehyde the evidence of this paper would support the "hydroxylation" theory, put forward many years ago and recently reaffirmed by Bone (*1*), in the statement that during the combustion of a hydrocarbon a peroxide may be formed after, or as a concomitant of an aldehyde, but not before.

ACKNOWLEDGMENTS

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Determination of 2,3-Butylene Glycol in Fermentations

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The production of 2,3-butylene glycol is a property common to many microörganisms in the dissimilation of carbohydrates and polyalcohols. The glycol has considerable potential commercial importance, awaiting only cheap production.

No rapid and accurate method has been described in the literature for the estimation of 2,3-butylene glycol and its quantitative determination has been a matter of concern to those working in the field of fermentations. It has in the past been determined quantitatively by two types of methods: gravimetrically, by isolation and direct weighing, and volumetrically, by oxidation either with a known volume of standard oxidizing agent or to a product which is determined subsequently.

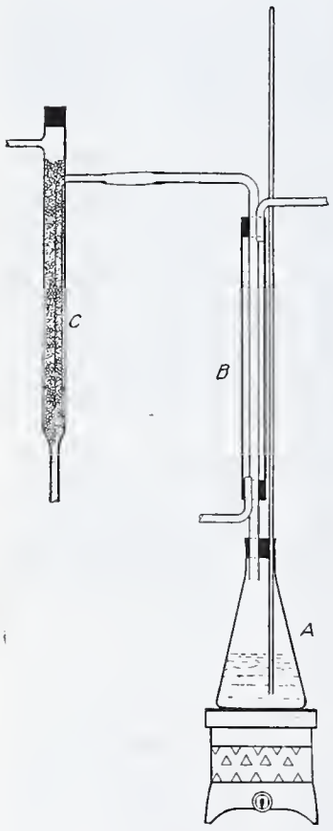

Figure 1. Apparatus

Obviously the first type of method as employed by Neuberg and Nord (*7*) and Breden and Fulmer (*2*) is difficult because of the necessity for a quantitative isolation of a pure product. The second type, oxidation of 2,3-butylene glycol, has been effected by bromine, potassium dichromate, and periodic acid. With bromine 2,3-butylene glycol is oxidized to diacetyl; the diacetyl is then determined by the use of Fehling's solution or by the nickel–dimethyl glyoxime method described by van Niel (*8*). Bromine oxidation has been found to give inconsistent results by Ruot (*10*), Donker (*3*), Breden and Fulmer (*2*), and Pederson and Breed (*9*). A method involving the oxidation of 2,3-butylene glycol, steam-distilled from wine, with a standard dichromate solution has been described by Fellenberg (*4*). This method involves several correction factors and is in general inapplicable to fermentation mixtures. The method suggested by Birkenshaw, Charles, and Clutterbuck (*1*) involving a general oxidation reaction of polyhydroxy alcohols with periodic acid as first described by Malaprade (*6*) appears to be the most satisfactory. This method, however, involves the extraction of an alkaline solution with ether and the estimation of the volume of standard periodic acid used in the oxidation of 2,3-butylene glycol according to the following reaction:

$$CH_3CHOH.CHOH.CH_3 + HIO_4 \longrightarrow 2CH_3CHO + HIO_3 + H_2O$$

Since 2,3-butylene glycol is only slightly soluble in ether, an extraction in order to be quantitative was found to require approximately one week, during which time a considerable volume of the fermentation mixture was carried over with the ether. The maintenance of a potassium periodate solution at constant normality is somewhat difficult.

The method here proposed involves the following reactions:

$$CH_3.CHOH.CHOH.CH_3 + HIO_4 \longrightarrow 2CH_3CHO + HIO_3 + H_2O$$
$$2CH_3.CHO + 2NH_2OH.HCl \longrightarrow 2CH_3CH = NOH + 2H_2O + 2HCl$$

The two molecules of hydrochloric acid are titrated with sodium hydroxide.

Procedure

A 20–50 cc. aliquot of the fermentation mixture (depending on the amount of 2,3-butylene glycol present) is placed in a 500-cc. Kjeldahl flask and 40 grams of anhydrous sodium carbonate are added. The sodium carbonate serves the dual purpose of preventing steam distillation of small quantities of lactic acid and of decreasing the solubility of 2,3-butylene glycol in water. During the distillation the volume is kept constant between 20 and 30 cc. One liter is distilled over, taking approximately 1.25 hours.

The hydroxylamine hydrochloride solution is standardized by bringing to neutrality to methyl orange, adding an excess of acetone, and titrating the liberated hydrochloric acid carefully with 0.05 *N* sodium hydroxide.

The apparatus consists of a 1-liter Erlenmeyer flask, *A*, to which is connected a reflux condenser, *B*, which passes into an absorption tower, *C*, containing a known volume of standard hydroxylamine hydrochloride solution. The whole apparatus is equipped for aëration either by air pressure or by suction.

An aliquot (500 cc.) of the steam distillate is placed in flask *A* and to this are added 10 to 15 cc. of concentrated sulfuric acid and 100 to 150 cc. of a potassium periodate solution containing about 3 grams of potassium periodate per liter. The reflux condenser is immediately installed and the absorption tower *C* connected. The contents of the flask are brought slowly to boiling (0.5 hour) and kept boiling for 2 hours, and during this time the apparatus is aërated at the rate of two bubbles per second. The absorption tower is then disconnected and the liquid contents poured into a flask. The tower is washed several times to insure the removal of all the uncombined hydroxylamine hydrochloride. To the hydroxylamine hydrochloride solution from the tower is added a solution of 0.1 *N* sodium hydroxide until neutral to methyl orange. Acetone (free from acid and alkali) is then added in excess to liberate hydrochloric acid and the volume of standard sodium hydroxide solution required to titrate the

hydrochloric acid liberated by the excess hydroxylamine hydrochloride is determined.

The molarity of the 2,3-butylene glycol solution present in the fermentation mixture equals

$$\frac{X-Y}{2\,F\,D}$$

in which X = cc. N $NH_2OH.HCl$ present in absorption tower C
Y = cc. N $NH_2OH.HCl$ remaining unused in absorption tower
F = cc. original fermentation
D = fraction of steam distillate used

This method was tried with solutions of 2,3-butylene glycol of known molarity. The results are shown in Table I. These solutions were made by dilution of a known weight of 2,3-butylene glycol extracted from fermentation mixtures and distilled three times within a temperature range of 1° C. However, the 2,3-butylene glycol used may not have been more than 96 to 97 per cent pure because of difficulties in its preparation.

Table I. Determination of 2,3-Butylene Glycol

2,3-Butylene-glycol Solution	Molarity	Cc. × Molarity	1 *M* Found	Accounted for
Cc.			*Cc.*	%
15	0.5	7.5	7.364	98.2
20	0.3	6.0	5.66	94.3
20	0.2	4.0	3.960	99.0
20	0.1	2.0	1.991	99.5
20	0.1	2.0	1.96	98.0
20	0.1	2.0	1.944	97.2
20	0.1	2.0	1.944	97.2
10	0.2	2.0	1.909	95.4
5	0.2	1.0	0.968	96.8
20	0.05	1.0	0.961	96.1
20	0.025	0.5	0.4987	99.7
5	0.1	0.5	0.4856	97.1
20	0.025	0.5	0.479	95.8
5	0.1	0.5	0.479	95.8
5	0.1	0.5	0.476	95.2
5	0.1	0.5	0.472	94.4
5	0.1	0.5	0.472	94.4
20	0.025	0.5	0.466	93.2
5	0.05	0.25	0.246	98.4
20	0.0125	0.25	0.233	93.2
				Average 96.44

The question arises as to what effect other substances present in the steam distillate of the fermentation mixture may exert on the results of the determination. The only compounds due to the presence of dextrose that might be found in the steam distillate, according to Fulmer and Werkman (*5*), are:

Acetaldehyde	2,3-Butylene glycol
Acetone	Ethyl alcohol
Acetylmethylcarbinol	Glycerol
Butyl alcohol	Isopropyl alcohol

Of these, butyl alcohol, ethyl alcohol, and glycerol are without effect (Table II).

Table II. Results Obtained by Substituting Various Substances for 2,3-Butylene Glycol

Substance	1 *M* Present	1 *M* Found	Accounted for
	Cc.	*Cc.*	%
Ethyl alcohol	330	0.3458	0.11
Isopropyl alcohol	261	0.3658	0.14
n-Butyl alcohol	211	0.1862	0.09
Glycerol	274	0.0665	0.02
Trimethylene glycol	263	1.4497	0.55
Acetylmethylcarbinol	...[a]	....	..

[a] See Table III.

Obviously acetaldehyde will affect the determination; however, in such fermentations as have been thus far studied it is present in such minute traces that its effects will be of no consequence.

Acetone will affect the results, if present; however, acetone and 2,3-butylene glycol rarely occur together in fermentation mixtures and may be easily separated by distillation before determination of the latter.

The effect of acetylmethylcarbinol appears to be of some special interest and significance in this determination because it is usually present along with the 2,3-butylene glycol. In order to determine this effect, some acetylmethylcarbinol was synthesized by the hydrolysis of the bromination product of methylethyl ketone. From this material was prepared a

Figure 2. Result of Application of Method to Fermentation Mixtures

solution of acetylmethylcarbinol, the molarity of which was determined by van Niel's method (*8*). A known volume of the acetylmethylcarbinol solution was treated in the manner described for 2,3-butylene glycol. The results shown in Table III indicate that any acetylmethylcarbinol present in the fermentation liquor will react in the procedure for 2,3-butylene glycol and must therefore be determined separately and subtracted from the total results given by our method. The acetylmethylcarbinol would be determined by the method of van Niel.

Table III. Determination of Acetylmethylcarbinol[a]

1 *M* Acetylmethylcarbinol	
Method of van Niel	Authors' method
Cc.	*Cc.*
0.2687	0.2786
0.8320	0.9010
0.2357	0.1944
0.1324	0.0998
0.1109	0.1591
1.5797	1.6329

[a] Assume reaction $CH_3.CHOH.CO.CH_3 \longrightarrow 2CH_3CHO$

It is evident, therefore, that the molarity of 2,3-butylene glycol in a fermentation mixture will be

$$\frac{X-Y}{2\,F\,D} - M$$

in which M = molarity of acetylmethylcarbinol.

This method has been applied to fermentation mixtures and the results obtained are illustrated by Figure 2.

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An Electrometric Method for Detection of Relative Freshness of Haddock

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During the course of an investigation conducted by the Bureau of Fisheries concerning the handling of fresh fish, it became highly desirable that an index as to the state of freshness of the samples to be examined be available. Such a test must not only be reliable, but also must not require too much time to execute. It is not necessary that such a test should tell how long it has been since the fish was caught, but it is important to obtain a knowledge of how much longer the fish may be expected to keep, if handled properly.

Since nearly all the work in the Gloucester, Mass., laboratory dealing with the handling of fresh fish has been with haddock, the test was designed to give a measure of the freshness of haddock only. While it seems probable that the results to be discussed might, in a modified form, be applicable to other varieties than the haddock, no comprehensive tests have been made with any other varieties.

Changes Occurring When Fish Decompose

Analyses (*3*, *7*) have shown that haddock consists of about 80 per cent water, 16.5 per cent protein, 1.25 per cent ash, and 0.3 per cent fat. The only substance whose decomposition is of any importance, during the spoilage of the flesh of these fish, is the protein. A measure of the protein hydrolysis or decomposition will give an indication of the freshness of the flesh.

One of the first changes occurring after the death of a fish is the onset of *rigor mortis*. Among a number of changes associated with *rigor mortis* may be mentioned an increase in lactic acid content and a very slight increase in hydrogen-ion concentration. Of course, the most noticeable change observed is that the fish becomes stiff.

Nothing definite can be said as to the duration of *rigor mortis*, or as to the time elapsing between the death of the fish and the onset of *rigor*. These seem to depend to a great extent upon a variety of factors, such as the method of capture and the temperature at which the fish is kept. However, it may quite generally be said that, if *rigor mortis* is present, the fish is of the highest quality.

While the fish is still in *rigor mortis* or immediately after it has passed off, a second process begins. All fish secrete certain enzymes, which during the life of the fish perform various normal functions. However, after death a process known as autolysis begins, and these enzymes start to hydrolyze the highly complex protein of the fish muscle into the simpler polypeptides, peptones, and amino acids.

A second process, usually accompanying autolysis, is bacterial decomposition. The first result of the action of bacteria is the formation of the same type of compounds as are produced during autolysis, such as polypeptides and amino acids. These, however, are only intermediate products which are later decomposed into a wide variety of substances. Many of these have disagreeable odors and some of them may be toxic. Most of the end products of bacterial decomposition of fish are basic, so that a rise in pH is observed. When bacterial decomposition occurs at low temperatures, as when the fish is packed in ice, the principal products seem to be the intermediate ones.

Although fish decomposition is usually classified as bacterial or autolytic, a more satisfactory basis, as far as a test for freshness is concerned, is based upon the type of products formed. Two types of changes occurring may be defined as follows: Primary changes are those changes in fish flesh which lead to the formation of amino acids from protein or to any intermediate products such as polypeptides and peptones. Secondary changes include those changes of the fish flesh which lead to the formation of products which detract from the value of the fish, usually contributing disagreeable flavors or odors. Some of these products are ammonia, amines, indole, hydrogen sulfide, and skatol.

There are two objections to the occurrence of primary change in the flesh of fish. First, as the protein molecule hydrolyzes, the fish becomes softer. In extreme cases juices run from the fish. These juices or "drip" contain dissolved protein, amino acids, and minerals. Such a condition, while detracting from the value of the fish, in no way has any actual harmful effect. The second objection is that a fish in which extensive primary changes have occurred is much more readily decomposed into secondary decomposition products when exposed to high temperatures and the action of bacteria. Gibbons and Reed (*11*) have shown that where extensive autolysis (largely primary changes) has taken place, the fish is much more rapidly decomposed by bacteria than is a fresh fish.

Secondary decomposition is generally considered to be the result of bacterial action. The end products of these reactions are chiefly basic. It is this type of decomposition which is usually considered as fish spoilage, and which renders it inedible.

When haddock are packed in ice, primary changes are the chief types of degradation occurring, at least until after the fish have been in ice for several weeks. After the haddock have been removed from the ice, secondary decomposition sets in very rapidly and true spoilage occurs. Since haddock are often packed in ice for about two weeks before they reach the consumer, the detection of the primary changes is of the highest importance.

Numerous tests for the degree of freshness of fish flesh have been proposed. Most of these depend upon the formation of some one end product of bacterial or enzyme action. Among these may be mentioned the test for hydrogen sulfide of Almy (*1*), and the test for ammonia of Tillmans and Otto (*16*). Other tests have been described by Fellers, Shostrom, and Clark (*9*), Clough (*8*), Tressler (*17*), Smith (*13*), Tauti, Hirose, and Wadi (*14*), Tillmans, Hirsch, and Kuhn (*15*), Benson and Wells (*5*), and Carey (*6*). Since these tests consider only secondary changes, and disregard the primary ones, their value is limited. An excellent discussion of the organoleptic list is given by Anderson (*2*).

Theory of the Method

In developing the present method, it was thought more advisable to follow the disappearance of the protein molecule than to observe the formation of any one end product. It was found that the buffer capacity (*18*) of a haddock solution decreased as primary changes occurred in the flesh. By choosing a pH range over which the buffer capacity of the inorganic constituents of the fish (mostly phosphate) was at

a minimum, a sensitive index of the primary changes was obtained. Such a range is between pH 6.0 and 4.2.

One of the principal products formed as a result of bacterial action is ammonia. By titrating the fish solution to a pH of 6.0 an indication of the amount of ammonia formed and hence the amount of secondary decomposition present is obtained.

The test then consists of titrating a fish solution first to about pH 6.0, then to about pH 4.3. The amount of acid used in the first step should be proportional to the amount of end products of bacterial decomposition, or secondary decomposition, and the amount of acid to go from pH 6.0 to pH 4.3 should be inversely proportional to the amount of primary changes or protein hydrolysis having taken place.

Method of Making the Test

At least 20 grams of the fish flesh, freed from all bones, should be ground as fine as possible in a meat grinder. Five grams of this are then weighed out and transferred to a 150-ml. bottle, 70 ml. of water are added from a graduated cylinder, and the bottle is stoppered and shaken for at least 10 minutes in a shaking apparatus. The contents of the bottle are then transferred to a 200-ml. Erlenmeyer flask, and an excess (about 0.3 gram) of quinhydrone added. The bottle is rinsed with 30 ml. of water, and the contents added to the flask. The flask and contents are shaken for an additional 2 minutes, and the contents then transferred to a 250-ml. beaker. A platinum electrode and saturated calomel half cell are then dipped in and connections made to a potentiometer. Readings are taken until a "constant" value is obtained. Successive portions of 0.0165 N hydrochloric acid are then added from the buret, stirring the solution and waiting for equilibrium to be attained between each addition. Several potentiometer readings are obtained between E = 0.200 and E = 0.100. The entire titration requires between 15 and 30 minutes. The acid should not be added too rapidly, especially between E = 0.140 and E = 0.170, since otherwise a drifting potential is obtained near E = 0.200. The amount of acid used to reach E = 0.100 (pH = 5.97) is calculated as well as the amount used to go from E = 0.100 to E = 0.200 (pH = 4.28).

The pH values given in the last sentence are calculated without regard to protein error. Care should be taken that equilibrium is always attained before taking a reading, since otherwise erratic results will be obtained. No absolutely constant e. m. f. is ever obtained. Usually there is a rapid fall to the point taken as the reading. The e. m. f. then slowly drifts, usually downward.

The amount of drift of potential varies with three factors. First, fresh fish produce less drift than stale ones. Second, after a large addition of acid, there is more drift than after a smaller addition. Third, at the end of the titration, near E = 0.200 volt, there is a considerably greater drift than at the beginning. With a little practice, it is not difficult to obtain the correct reading.

The drift of potential seems to be caused by the presence of some of the fish protein suspended in the solution, since with filtered solutions very little drift occurs. However, the solution cannot be filtered, since the sensitivity of the test depends upon the presence of these suspended particles which contribute to the buffer capacity.

This test was run on a large number of samples of fish preserved in various ways. Some fish were packed in ice whole, and a separate fish withdrawn for each test. In other cases the fish was cut into small pieces, wrapped in moisture-proof cellophane, and packed in ice. In still other cases the fish was ground and stored at various temperatures.

Interpretation of Results

In all the following discussions, the value of B will be taken as the number of milliliters of 0.0165 N hydrochloric acid required to bring the pH of 5 grams of fish in 100 ml. of water to 6.0. More exactly, since these pH values neglect protein error, the value of B is the number of milliliters of 0.0165 N hydrochloric acid required to bring the electromotive force to E = 0.100 volt, using the technic described. This is assumed to be proportional to the amount of secondary decomposition present.

In a similar way the value of A is defined as the number of milliliters of 0.0165 N hydrochloric acid required to change the E value from 0.100 to 0.200 volt. This corresponds to a pH change of from about 6 to 4.3, and is inversely proportional to the amount of primary changes present in the fish.

Table I. E. M. F. Obtained after Addition of Hydrochloric Acid to Fish Solution

Acid Added	Time Solution Stood after Last Acid Addition	E. M. F.
Ml.	*Minutes*	*Volts*
0	0	0.075
0	0.25	0.070
0	1	0.055
0	2	0.054
0	3	0.054[a]
0	5	0.054
8.0	0	0.1025
8.0	1	0.099
8.0	2	0.0975
8.0	3	0.0975[a]
8.0	4	0.0970
8.0	7	0.0965
9.0	0	0.1060
9.0	0.5	0.1055
9.0	1	0.1050
9.0	2	0.1050[a]
20	0	0.176
20	1	0.172
20	2	0.169
20	3	0.167
20	4	0.166
20	5	0.165
20	6	0.164
20	7	0.163
20	8	0.1625[a]
31	0	0.199
31	1	0.196
31	2	0.195
31	3	0.194
31	4	0.194[a]
31	5	0.1935
31	6	0.1930
35	0	0.212
35	1	0.210
35	2	0.210[a]
35	3	0.2095
35	4	0.2095
35	5	0.2090

[a] E. M. F. taken as the reading.

The following data show the average values of A for haddock kept packed in ice from the time they were caught, samples being removed for analyses at the intervals indicated. The results are the average of about 200 determinations. The last column shows the maximum deviations which can be obtained for different samples of haddock in identical stages of decomposition.

Table II. Average A Values for Haddock Packed in Ice

Days in Ice	Condition	A	Maximum Error
0.25 (6 hours)	Fresh, stiff	26	0.3
1	Fresh, stiff	31	0.3
2	Fresh, slightly stiff	27.5	0.3
3	Fresh	26	0.3
4	Fresh	24	0.4
6	Fresh, slight sweet odor	22.5	0.4
8	Somewhat sweet odor, slightly soft	20	0.5
12	Sweet odor, a little soft	19	0.6
18	Very sweet odor, soft	17	0.8
21	Intense sweet odor, very soft	15	1.0

From these data it will be seen that a fresh fish about 6 hours out of the water has an original A value of about 26, and that this value rises, as *rigor mortis* appears. As *rigor mortis* passes off, the value of A diminishes from a maximum of about 31 to a minimum of about 15. The decrease in accuracy with increase in decomposition is due to the greater difficulty of obtaining a constant e. m. f. for stale fish.

TABLE III. CONDITION OF HADDOCK PACKED IN ICE AS INDICATED BY ELECTROMETRIC METHOD OF DETECTING DECOMPOSITION

Description of Fish Indicated by A Values			Description of Fish Indicated by B Values When Associated with Corresponding A Value											
			B = 4 to 6		B = 6 to 8		B = 8 to 10		B = 10 to 12		B = 12 to 14		B = 14 to 17		B = more than 17	
A values	Time since caught	Extent of primary change	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor	Extent of secondary change	Possible odor
	Days															
32–25	0–3	None	None	Fresh	None	Fresh	Slight	Slightly fishy	Small	Fishy	Pronounced	Stale	Considerable	Very stale	Extreme	Putrid
25–22	3–6	Slight	None	Fresh	None	Fresh *Slightly sweet*	Slight	Slightly fishy *Slightly sweet*	Small	Fishy *Slightly sweet*	Pronounced	Stale	Considerable	Very stale	Extreme	Putrid
22–20	6–10	Small	None	Fresh *Slightly sweet*	Slight	Slightly fishy *Slightly sweet*	Small	Fishy *Slightly sweet*	Small	Fishy *Definitely sweet*	Pronounced	Stale	Considerable	Very stale	Extreme	Putrid
20–18	10–14	Pronounced	None	Fresh *Slightly sweet*	Slight	Slightly fishy *Definitely sweet*	Small	Fishy *Definitely sweet*	Pronounced	Stale *Definitely sweet*	Considerable	Very stale	Extreme	Putrid	Extreme	Putrid
18–16	14–18	Considerable	None	Fresh *Definitely sweet*	Slight	Slightly fishy *Extremely sweet*	Small	Fishy *Extremely sweet*	Pronounced	Stale *Extremely sweet*	Considerable	Very stale	Extreme	Putrid	Extreme	Putrid
16 or less	Over 18	Extreme	Slight	Slightly fishy *Extremely sweet*	Small	Fishy *Extremely sweet*	Pronounced	Stale *Extremely sweet*	Considerable	Very stale	Extreme	Putrid	Extreme	Putrid	Extreme	Putrid

One cause of the initial rise in the A value is the formation of lactic acid. The presence of lactic acid tends to increase the A values in two ways. First it acts as a buffer to some extent around a pH of 4.3, thus requiring more acid to reach this pH value and increasing A. Moreover, Beatty (*4*) has shown that when lactic acid forms, the protein becomes more soluble. Since the protein, itself, acts as a buffer, an increase in protein solubility increases the buffer capacity, and hence the value of A.

Sharpe (*12*) and Fiske and Subbarow (*10*) have shown that certain phosphorus-containing organic substances are converted into orthophosphates after the death of the fish or animal of which they are a part. Since orthophosphates act as buffers to a small extent over the pH range of the A value, the formation of phosphates may be a contributing factor to the initial rise in the value of A.

The exact cause of the fall of the A value as primary decomposition proceeds is uncertain, but may be due in part to a change in solubility of the protein. It has been shown that when a frozen fish is stored, a transformation of a part of the fish protein to a less soluble form occurs. It is possible that such a reaction occurs in the case of fish packed in ice. Another possibility is that the buffer capacity of the primary decomposition products of the fish over the pH range measured is less than that of the protein in the fresh fish.

However, whatever the exact cause may be, it is certain that during primary decomposition the protein molecule does break down into simpler compounds, and that accompanying this change a loss in buffer capacity of the fish suspension over the pH range 4.3 to 6.0 simultaneously occurs.

The initial rise in the value of A from 25 to 31 followed by its decrease makes all the values of A between 25 and 31 correspond to two conditions of the fish. However, this is of no practical importance. The initial rise in the value of A is very rapid, a value of 31 usually being reached in less than 24 hours. Moreover, fish in which the value of A is rising are in the state of *rigor mortis* which can readily be recognized. Therefore, since haddock are almost invariably one day old before they are landed, the initial rise in the values of A can be neglected. Usually haddock obtained from gill netters, the freshest of any, have an A value no higher than 28 and the value is falling. For trawl fish the value is ordinarily around 23.

When a haddock is first caught, it probably has a B value between 7 and 8. If no pronounced bacterial decomposition sets in, the value of B falls to a minimum of 5 when lactic acid forms, and the protein begins to hydrolyze. This initial fall in the value of B is due to the combined effect of the formation of lactic acid, and the consequent lowering of the pH, and to the loss of buffer capacity of the flesh. In the initial stages of hydrolysis, any value of B less than 8 may be said to indicate a fish in which no marked bacterial decomposition has occurred. However, a haddock which has been caught quite recently, and has an A value of 24 or more, should not have a B value of more than 8. If the value of B in such a case does exceed 8, suspicion is raised that the fish has at some previous time been allowed to stand at too high a temperature.

If a haddock is allowed to spoil while packed in ice, the actual spoilage, as indicated by the formation of a putrid odor, does not occur until after three weeks or more. Usually after this time offensive odors develop rapidly. Simultaneously the value of B, which up till then has not exceeded 8 or 9, sharply rises to 12 or more. In case the spoilage occurs at a higher temperature, the value of B rises more rapidly, a value of 20 being reached in extreme putrefaction. In such a case a value of about 15 indicates the fish to be barely edible.

In interpreting the results of this test, it is necessary to consider the values of both A and B. The value of either alone is meaningless. The chart (Table III) assumes that maximum rigor has been reached or passed away. For haddock, this condition will virtually always be realized. The estimate of the time since the fish had been caught assumes that the fish was well packed in ice since catching. This value is necessarily only approximate. The probable odors which definitely accompany the varying degrees of secondary change are given, and the italics indicate a second type of odor which can be detected when sufficient primary change has taken place and the odor due to secondary change is not too intense.

No attempt has been made to determine the amount of decomposition or changes which must be present to make a fish inedible. This is largely a matter of personal opinion, and the establishment of any A and B values as a limit for a fresh fish would be purely arbitrary. Such a procedure is beyond the scope of this paper.

Test Based on Conductometric Titration

An attempt was made to develop a conductometric titration, to replace the potentiometric determination of the amount of primary decomposition present in the fish. Enough acid was added to a 5-gram sample of the fish suspended in water to bring the pH to 6.0. The conductivity was then determined, a definite quantity of acid added, and the increase in conductivity ascertained. This increase in conductivity, designated by R, should be proportional to the value A. This was found to be reasonably true, as can be seen from the following data:

Table IV. Results of Conductometric Titration

A	R	Condition
29.0	23.0	Very fresh, still slightly stiff, fresh odor
26.1	21.3	Fresh
24.8	31	Fresh, sweet odor, slightly soft
23.9	29	Fresh, slightly fishy odor
22.5	20.2	Fairly good condition, sweet odor, slightly soft
20.7	41.7	Fairly good condition, fresh odor, quite soft
17	65	Stale, very soft
15.8	36.3	Very sweet odor, soft
15.6	40.5	Extremely sweet odor, stale, soft

The method is extremely simple, requiring only about 3 minutes to execute. However, it cannot be recommended for a test, since differences in initial conductivity caused by brining the fish before the test was made (a common commercial practice) cause large deviations in the results.

While this test has been applied principally to fresh haddock, the authors are of the opinion that a great variety of applications are possible. The tests have also been applied to cod and pollock with results indicating that it is applicable. It is possible that the method may be applied in the case of various meats and packing house products.

Summary

A reliable test for the freshness of fish has been described, based on buffer capacity measurements. The test requires less than one hour to perform. It gives information, not only as to the accumulation of bacterial end products, but, what is even more important, as to the amount of protein breakdown taken place.

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Determination of Zirconium in Steels

Selenious Acid Phosphate Method

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In a previous paper (*1*) the selenious acid method for zirconium (*2, 3*) was shown to be applicable to the determination of zirconium in alloys. It was shown, however, that tungsten may be brought down with the final precipitate and an additional step in the procedure was found necessary. In view of the fact that those elements which tend to cause interference in the selenious acid method do not do so in the phosphate method, and vice versa, it seemed advisable to attempt to combine the two methods in the hope of obtaining a rapid, reliable method for zirconium in alloys in the presence of any element which might ordinarily be present. By thus combining these two procedures, a double precipitation of zirconium is made (advantage over the usual phosphate method) and tungsten and other elements should not interfere (advantage over the plain selenite method). As to the order of precipitation, the difficulty of dissolving a zirconium phosphate precipitate would indicate the desirability of precipitating the zirconium first as selenite and then as phosphate rather than in the reverse order. By using this order the zirconium selenite is dissolved in fairly concentrated sulfuric acid in which it is readily soluble, rather than in dilute hydrochloric acid, in which (as in the case of the plain selenite method) it sometimes dissolves with difficulty.

Proposed Method

Dissolve 3 grams of steel in 40 cc. of concentrated hydrochloric acid. When solution is complete or nearly so, add sufficient concentrated nitric acid to oxidize the iron. Evaporate to dryness on the steam plate, moisten the residue with 6 *N* hydrochloric acid, evaporate to dryness, heat at 105° C. for 30 minutes, and treat with 30 cc. of 6 *N* hydrochloric acid and 50 cc. of hot water. After all soluble salts have dissolved, filter and wash the residue with dilute hydrochloric acid and finally with hot water. Treat the filtrate and residue (each of which may contain zirconium) separately as follows:

Filtrate. Evaporate the filtrate nearly to dryness, add 40 cc. of 6 *N* hydrochloric acid, and extract twice with 40 cc. of alcohol-free ether to remove the greater part of the iron. Evaporate the aqueous solution to complete dryness, dissolve in 12 cc. of 12 *N* hydrochloric acid, dilute to 400 cc., heat nearly to boiling, add 15 cc. of 3 per cent hydrogen peroxide to prevent the precipitation of titanium, and 20 cc. of a 10 per cent solution of selenious acid. Allow to stand until any precipitate has coagulated. Filter, wash with hot water, and unite with the corresponding precipitate obtained from the residue below.

Residue. Ignite the siliceous residue in platinum. Treat with sufficient hydrofluoric acid (and two drops of concentrated sulfuric acid) to volatilize the silica. Evaporate to dryness and fuse with sodium carbonate. Extract with hot water, filter, wash with dilute sodium carbonate solution and then with hot water. Ignite the residue and fuse with potassium pyrosulfate. Dissolve in 100 cc. of hot water containing a few drops of sulfuric acid, make ammoniacal, filter, wash with hot water, and dissolve the precipitate in 25 cc. of 6 *N* hydrochloric acid. Dilute to 400 cc., heat nearly to boiling, add 15 cc. of 3 per cent hydrogen peroxide and 20 cc. of 10 per cent selenious acid solution, and allow to stand until the precipitate has coagulated. Filter, wash with hot water, and unite with the corresponding precipitate obtained from the main filtrate.

Dissolve the combined precipitates in 50 cc. of 18 *N* sulfuric acid, dilute to 200 cc., warm to 50° C., add 20 cc. of 3 per cent hydrogen peroxide and 50 cc. of a 20 per cent solution of diammonium phosphate, precipitating zirconium phosphate. Allow to stand 2 hours, filter, wash thoroughly with a 5 per cent solution of ammonium nitrate and ignite slowly. Gradually raise the temperature to the full heat of the Tirrill burner and weigh as ZrP_2O_7.

Results by Proposed Method

In the analyses made by the proposed method, 3 grams of a plain carbon steel were dissolved and to the solution were added measured amounts of zirconyl chloride solution corresponding to 0.11, 0.28, and 1.41 per cent of zirconium in the original steel. In addition, 20 mg. each of other metals in the form of solutions of their salts were added. The results obtained are shown in Table I.

Table I. Analysis of Plain Carbon Steel Samples by the Selenite-Phosphate Method

(Sample = 3 grams)

Constituents Added	Zirconium Found: Zr present = 0.0034 gram, 0.11%		Zr present = 0.0085 gram, 0.28%		Zr present = 0.0423 gram, 1.41%	
	Gram	%	*Gram*	%	*Gram*	%
None	0.0033	0.11	0.0083	0.28	0.0424	1.41
	0.0034[a]	0.11	0.0083[a]	0.28	0.0420	1.40
Ti^{++++}, UO_2^{++}, VO_3^-	..	..	0.0086	0.29	0.0423	1.41
WO_4^{--}	0.0032	0.11	0.0086	0.29	0.0423	1.41
	..	..	0.0087	0.29	0.0430	1.43
	..	..	0.0081	0.27	..	..
WO_4^{--}, Ti^{++++}, UO_2^{++}, VO_3^-	..	..	..	..	0.0420	1.40
WO_4^{--}, Cr^{+++}, VO_3^-	0.0033	0.11	0.0079	0.26	0.0424	1.41

[a] Bureau of Standards cast iron No. 74 (0.464 per cent P).

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Windshield for Saybolt Viscometer

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Because of air currents which cannot be readily avoided in a large laboratory, the use of a windshield has been found desirable in the determination of the viscosity of lubricating or fuel oils. The fine stream of oil is otherwise blown out or around the opening of the cup. Temporary shields of cardboard have been utilized with rather unsatisfactory results.

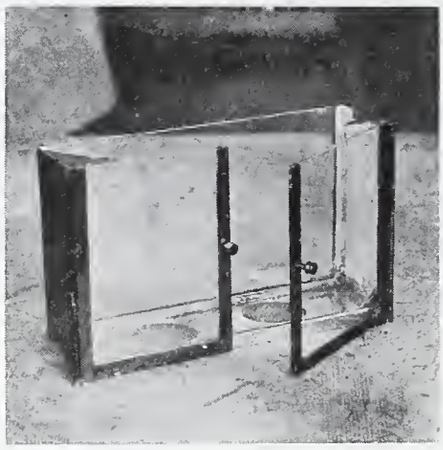

Figure 1

A neat and efficient shield (Figure 1) may readily be built to fit beneath the American Instrument Company's Saybolt viscometer (Figure 2). Ordinary window glass, machine screws, piano hinges, and galvanized sheet iron may be utilized. The shield is built around the cup holder and the glass may be easily removed for cleaning or replacement. The hinged doors give free access to the cups and may be closed at the start of the determination.

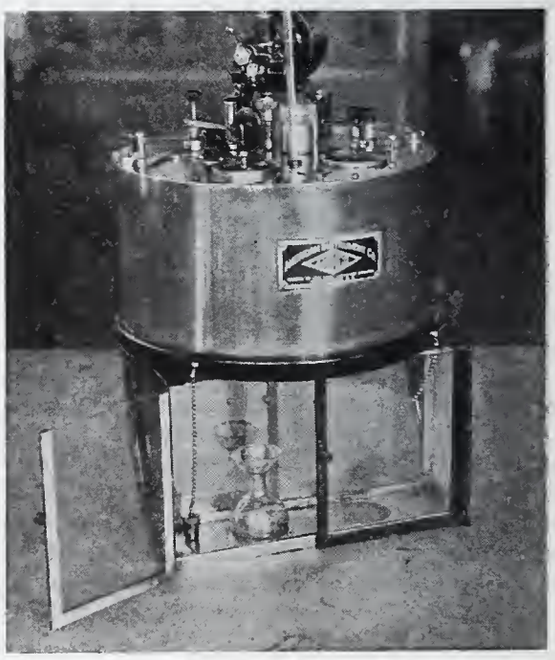

Figure 2

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A Continuous Extractor of Large Capacity

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A CONTINUOUS extractor that will hold 10 to 45 kg. (20 to 50 lb.) of material at one charge is very useful in most biochemical and nutrition laboratories. The extractor shown in Figure 1, which has been designed for this purpose, consists of an earthenware jar, *J*, with a ground top of special design. The top contains two 3.3-cm. (1.25-in.) holes for the condensers *A* and *B*, as well as three special knobs for imbedding bolts. The bolts are set by placing

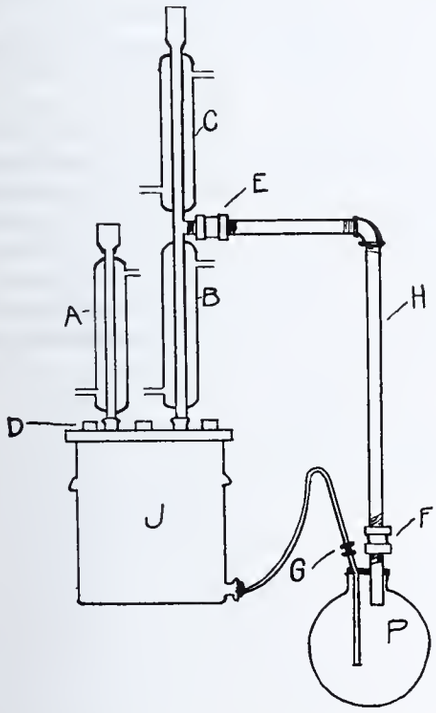

Figure 1. Diagram of Assembled Extractor, without Steam Bath and Supporting Bracket

them in position and then pouring the holes around them full of molten lead. No gaskets are needed, since the ground top is quite wide. A beveled edge has not been used, but might be useful if not too expensive.

Above *B* a second condenser, *C*, is p'aced and the vapor line is introduced between these two condensers. If it is desired to carry out a hot extraction with some solvent such as alcohol, the water of the lower condenser, *B*, is shut off. The earthenware jar makes it possible to carry out either hot or cold extractions. The condensers, *B* and *C*, consist of a piece of brass pipe an inch in diameter. The jackets consist of iron pipe. The vapor line, *H*, is copper tubing with a diameter of 1.9 cm. (0.75 in.). The siphon tube, *G*, is a copper tube 0.5 cm. (0.374 in.) in diameter. Connections are placed at *E*, *F*, and *G*. With a 20-liter (5-gal.) jar, *J*, a 22-liter Pyrex flask, *P*, is large enough. A couple of rings of garden hose form a very satisfactory support for this flask in the steam bath.

Figure 2 shows the extractor after a year of constant use. The iron bracket to which the top of the jar is bolted has an upright rod welded to it, serving as a support to which the condensers are clamped. In this photograph the condenser *A* (Figure 1) was lifted to permit a clear view of the iron tripod.

When the extractor is in use a rope leading to an ordinary pulley is fastened to the bracket at the point where the upright support is attached, making it possible for one person to operate the extractor.

After the extractor is assembled it is disconnected at point *E*. The lid bearing the condensers is lifted enough for clearance and swung free from the opening of the jar. The material to be extracted is placed in a cloth bag and lowered

Figure 2. Extractor, Showing Iron Bracket for Moving Lid

into the jar, and the lid is then swung back and lowered into position. Allowance must be made for swelling after the solvent is placed over such material as casein.

This extractor is simple in design, operates effectively and easily, and is inexpensive.

Acknowledgment

The author wishes to thank the Maurice A. Knight Company for manufacturing these special jars from his design.

Received January 28, 1933.

Progress toward Industrialization in Mexico is noted in activities centering around Mexico City, from where also reports come concerning federalization of the country's textile industry in accordance with a legislative enactment of March 20, 1933.

Certain Mexico City industrialists are reported to be planning an organization under central management to produce a diversified line of goods, such as hennequen bags, incandescent lamps, rubber articles, such as fountain pens and combs, and Cellophane and rayon yarn.

A large carbide plant near Mexico, inactive since the World War, is producing a satisfactory grade of carbide from raw materials obtained nearby. The plant is said to have a capacity of 5000 tons annually. The present consumption of the country is estimated at 3500 tons.

Photoelectric Colorimeter for Measuring Color Intensities of Liquid Petroleum Products

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Commercial colorimeters for measuring the color of petroleum products depend on visually matching the unknown with some standard scale of color. As the standards rarely match the unknown with respect to all the attributes of color—hue, saturation, and brilliance—a large personal equation is introduced, which leads to erratic results. A simple photoelectric colorimeter has been constructed which completely removes the human equation and still grades the colors closely in accordance with normal visual sensation. Petroleum refining operations involving the measurement of color may now be studied more precisely because of the greater accuracy of this method.

In the petroleum industry it is necessary to measure what is usually called the "color" of various oils, both for purposes of controlling refinery operations and for the final production of oils sold under a color specification. Many methods have been proposed for color measurement and several are used for this purpose. Most of them are based on visual sensation wherein the attempt is made to match the color of the oil with a colored glass, or possibly with a solution of iodine or other colored substance. The oil is then given a color value in terms of the scale of colored glasses or solution strength which seems most closely to match it. These values are arbitrary, depending on the method. In use, such methods are simple and rapid but generally inaccurate, because the oil rarely matches the colored glass or solution with respect to the three recognized factors in color sensation—hue, saturation, and brilliance. Hence the result reported depends to a considerable extent on which of the three components of color sensation has the greatest appeal to the operator.

Petroleum products vary from water-white to black, passing through various shades of yellow, orange, and red. No definite absorption bands appear in the visible spectrum. In passing from water-white, the first loss of transmittance appears in the violet, which, as the color increases, moves progressively toward the red. When the per cent transmittance is plotted against the wave length of the light, the slope of the curve is not very steep as compared to similar curves for many of the dyes. An oil may or may not approach 100 per cent transmittance at the longer wave lengths, depending on its source and refinement, and the slope may vary for the same reasons. It is evident, then, that for equal brilliance, oils may vary considerably in hue and saturation. For this reason it has been practically impossible to measure color visually as a single value representing sensation with any accuracy, because different operators do not react the same to variations in hue and saturation, nor does a good solution of the problem seem probable as long as there is a personal equation in the determination. Therefore, the measurement of color of petroleum oils in the past has in reality been an attempt to measure brilliance, which was then arbitrarily converted to a so-called "color" scale.

Photoelectric Cell

The photoelectric cell has often been proposed as a means of eliminating the personal equation, but for various reasons no practical method based on use of such a cell has been adopted in the petroleum industry. However, a photoelectric cell has recently been put on the market (photronic cell, model 594, manufactured by the Weston Electric Instrument Co.), which combines to a remarkable degree the characteristics required to evaluate color sensation or, more accurately speaking, brilliance. The most important consideration here is that the relative sensitivity for hue should be approximately the same as the human eye. Figure 1 illustrates the remarkable similarity for this cell and the normal eye. This means that, regardless of the spectral distribution of the light transmitted by two substances, if the eye perceives one to be darker than the other, the cell will grade them in the same order. The somewhat higher sensitivity in the region of 4500 Å. will, of course, cause the cell to grade certain light-colored oils slightly different from the eye, but for practical purposes this is not serious with petroleum oils. Darker oils have little or no transmittance in this region, so that what appears to be a substantial difference in response is in reality of small consequence with most of the petroleum products.

This photoelectric cell possesses other characteristics which greatly simplify its adoption to color measurement. It generates its own current in amounts sufficient to be measured directly, the output being about 1.4 microamperes per foot-candle. Its response is quick and it stabilizes rapidly without fatigue. It is small, rugged, and inexpensive.

One of the essential features in a colorimeter is the reproducibility of the results obtained. Not only should a single instrument reproduce itself, but for its wide applicability it must give concordant results with all others of the same type. According to the claims of the manufacturers of the above photoelectric cells, the spectral response curve of the cells can be reproduced within 1 per cent of the average, which is more than sufficient for practical color measurements. The results obtained in the authors' laboratories with different photoelectric cells of the kind described are in substantial agreement with these claims.

If a light source of suitable and uniform intensity is placed at a short distance from a photoelectric cell, the cell will generate some current. If the intensity of the light falling on the cell is changed by increasing or decreasing the distance between the cell and the lamp, the current will be respectively less or greater. If the light remains stationary but a glass cell containing oil or some other transparent colored substance is introduced between the photoelectric cell and the light, the current will decrease because some light will be

reflected and absorbed by the glass cell and its contents. If now the lamp is brought nearer to the photoelectric cell, the current generated can again be brought to its original value and the quantity of light absorbed by the glass cell and its contents can then be evaluated in terms of the distance it was necessary to move the light to attain the desired effect.

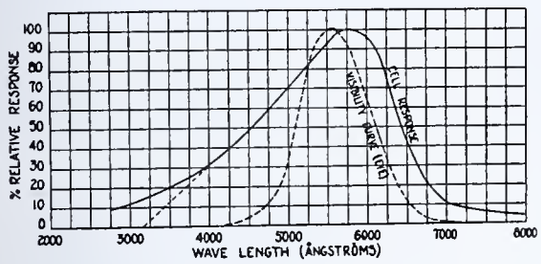

Figure 1. Spectral Response of Weston Photronic Photoelectric Cell

The discussion above shows that the color of the oil, as measured by the photoelectric cell, might be expressed either as a function of the current with a stationary source of light, or as a function of the distance, if the light is movable. The latter arrangement was preferred in constructing the colorimeter, as it does not require a calibrated microammeter, and as it permits compensations for slight changes in the sensitivity of different photoelectric cells, lamps, or ammeters.

Set-Up of Colorimeter

The colorimeter, which has been successfully used in the authors' laboratories for a number of months, is shown diagrammatically in Figure 2. It consists essentially of a photoelectric cell connected with a microammeter, an oil cell, and a uniform source of light. The photoelectric cell has already been discussed, and does not require further description.

The oil cell is 5.2 mm. in depth and 50 mm. in diameter. The diameter is immaterial, providing it completely covers the face of the photronic cell. While the depth may be varied also, a standard depth must be established eventually in order to provide complete agreement with different instruments on all oils.

The light source is a 100-watt, 115-volt Mazda projection lamp, manufactured by the General Electric Company. Deviations from the above specifications are allowable without greatly changing the results, provided the spectral energy distribution of the light source remains about the same. Theoretically, the spectral energy distribution of daylight is desirable in a light source for color work. However, it was found experimentally that the above-named lamp answers the practical requirements. It does not show any appreciable loss in intensity when operated at 105 volts, even after several months of service, and different lamps of the same type give color readings which closely agree among themselves. It is essential, however, to operate the lamp at a constant voltage (105-volt current is employed) to insure uniform results.

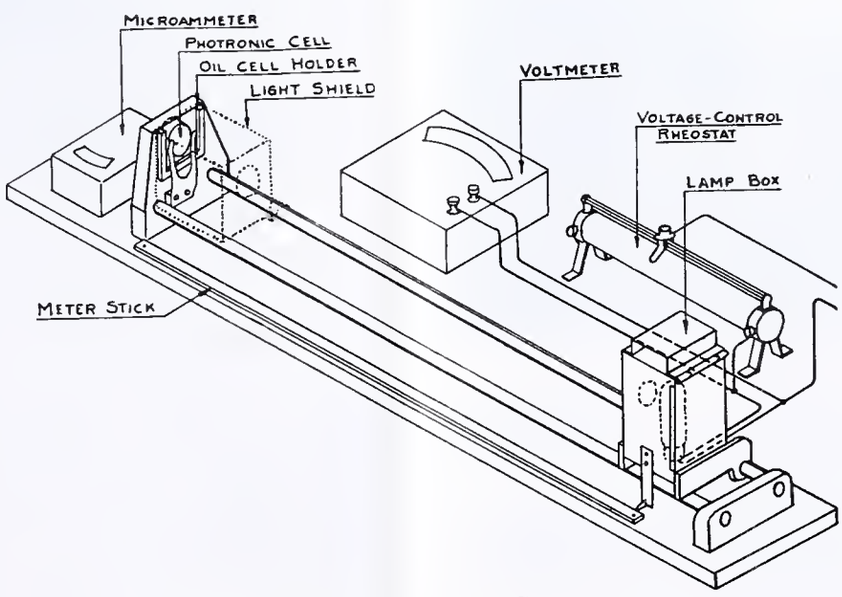

Figure 2. Photoelectric Colorimeter

In setting up the colorimeter, the photoelectric cell was made stationary and attached to the frame of the instrument. The oil cell was fastened directly in front of the photoelectric cell, also in a fixed position. The lamp was made movable, in order to vary at will the intensity of light falling on the oil cell. A special shield was provided in front of the photoelectric and oil cells, to eliminate the possibility of errors due to the reflection of light from the walls of the room or from the nearby objects. In later designs, it was found preferable to make the lamp stationary and the cells movable and to enclose the whole instrument in a light-proof cover.

Operation of Colorimeter

In operating the instrument, the oil cell is first filled with a medicinal or similar oil of 30+ Saybolt color. The lamp is placed at its maximum distance from the photoelectric cell, which was originally 100 cm. but shortened to 50 cm. in later designs. By properly adjusting the depth of the oil cell, this shortening was accomplished without decreasing the working range of the colorimeter. The reading of the microammeter connected to the photoelectric cell is then taken and is used as the standard reading. This reading includes compensations for variations in sensitivity of different photoelectric cells, lamps, or ammeters and also for reflections at the glass-air and glass-oil interfaces. Theoretically, this last compensation is altered somewhat by the intensity of the light falling on the cell and therefore varies with the position of the lamp. However, in practice this is of no importance. The amount is small and it cancels out in the final results because they are comparative and not absolute.

After obtaining the standard microammeter reading, the oil cell is filled with oil of unknown color. The lamp is then moved towards the cell until the microammeter gives a reading equal to the standard. The distance between the photoelectric cell and the lamp is determined and taken as the measure of the color intensity of the unknown oil.

It is evident that the "color" indicated by the photoelectric colorimeter is in reality not the measure of the color or hue of the oil but the measure of its brilliance. Brilliance is defined as that attribute of color in respect to which it may be classed as equivalent to some number of a series of grays ranging between black and white, and, therefore, the photoelectric colorimeter is capable of grading the oils only into darker and lighter ones as they appear to the eye. This cannot be accomplished successfully by the present methods of measuring the color of oils. An oil which appears darker to the eye will also be graded darker by the photoelectric colorimeter but not necessarily so by the other types of colorimeters now in use.

The intensity of illumination is inversely proportional to the square of the distance from the point source of light. In order to verify how closely the photoelectric colorimeter follows this law, a flicker-wheel was introduced between the lamp and the photoelectric cell. The oil cell was filled in these experiments with a

medicinal clear oil, although it was found that the readings which were obtained in presence or absence of the oil cell were identical, provided the standard ammeter readings were properly adjusted. Table I shows a very good agreement between the calculated and experimental values. The agreement is believed to be within the limits of the experimental error involved in these measurements and more

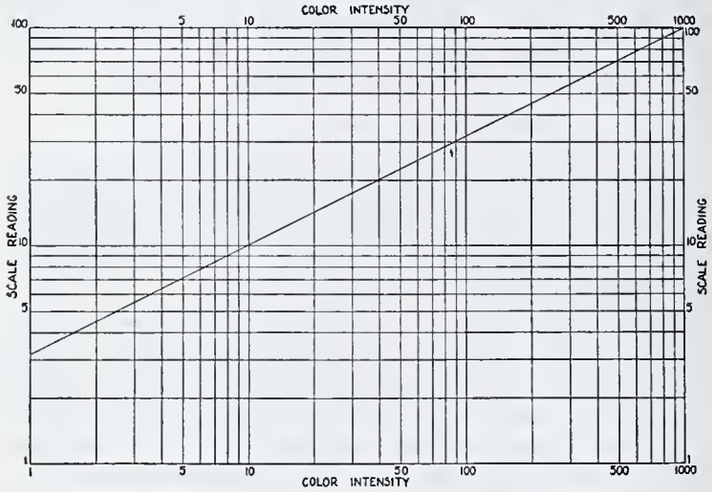

Figure 3. Calibration of Photoelectric Colorimeter with Flicker Wheels

than sufficient for practical purposes. It has also been found that the variation of the correction factor for the reflection of light from the oil-glass and glass-air interfaces at various distances of the lamp from the photoelectric cell is too small to be of importance and can, therefore, be neglected.

Table I. Theoretical and Experimentally Determined Distances of the Photoelectric Colorimeter Corresponding to Equal Transmittances of Light

Light Transmitted (Measured by flicker-wheel)	Distance Calculated	Distance Observed
%	*Cm.*	*Cm.*
100	100.0	100.0
90	94.8	93.6
80	89.4	87.7
70	83.7	81.8
60	77.5	75.7
50	70.7	69.0
45	67.1	65.2
40	63.2	61.0
35	59.2	57.2
30	54.8	53.0
25	50.0	47.8
20	44.7	43.5
15	38.7	37.0
10	31.6	30.3
6	24.5	24.0
4	20.0	19.5
2	14.1	14.0

On the basis of these findings it is simple to calibrate the instrument in terms of visual brilliance, by taking the square of the distance between the photoelectric cell and the position of the lamp at the point at which the reading is taken. For this purpose, however, the distance should be expressed as a per cent of the maximum distance of the lamp from the photoelectric cell. It is therefore preferable to divide this maximum distance into one hundred equal parts instead of measuring it in generally accepted units of length, such as centimeters, inches, etc. The resulting equation connecting the distance D and brilliance B

$$B = AD^2$$

(where A is a constant depending on the units chosen for expressing brilliance or distance) can be easily expressed graphically as a straight line on double logarithmic paper.

The calibration of the instrument on the basis of the above scale, which might be designated as the brilliance scale, is not suitable for industrial use, as refinery men are generally accustomed to speak of the color of the oil and not its reciprocal brilliance. In practice this is easily accomplished by reversing the scale of the colorimeter and placing the one hundred and not the zero point at the photoelectric cell. The resulting scale, which is designated as the color intensity scale, is shown on Figure 3. It is evident that it bears the same simple relationship to the distance as the brilliance scale and is also plotted as a straight line on double logarithmic paper, because the only difference introduced in the above formula is the substitution of $(100 - D)^2$ for D^2. In order to express the color intensities in some convenient units, the color intensity corresponding to the theoretical position of the lamp in direct contact with the photoelectric cell was assigned a value of 1000.

Table II. Color Intensities of Iodine–Potassium Iodide Solutions[a]

(Solutions contain potassium iodide double by weight of iodine)

Iodine Concentration	Distance from Lamp to Photronic Cell
Mg./10 cc.	*Cm.*
1.60	93.0
3.20	90.5
3.40	90.8
4.48	88.5
6.50	86.0
10.05	83.0
13.0	80.2
13.8	79.5
15.0	78.5
50.0	61.7
60.0	59.2
210	41.5
281	37.0
282	38.2
305	36.7
581	29.4
663	28.4
1270	23.0

[a] Specific gravity of these solutions is fairly closely represented by the formula: $S = 0.997 + 0.0002312I$, where S = sp. gr. at 25° C. and I = iodine concentration in milligrams per 10 cc. of solution.

An attempt was made to calibrate the photoelectric colorimeter in terms of iodine solutions of known concentrations. Solutions containing iodine and double its amount by weight of potassium iodide were used. Iodine was selected, as the iodine colors are more or less familiar to petroleum chemists and as this substance is easily obtained in

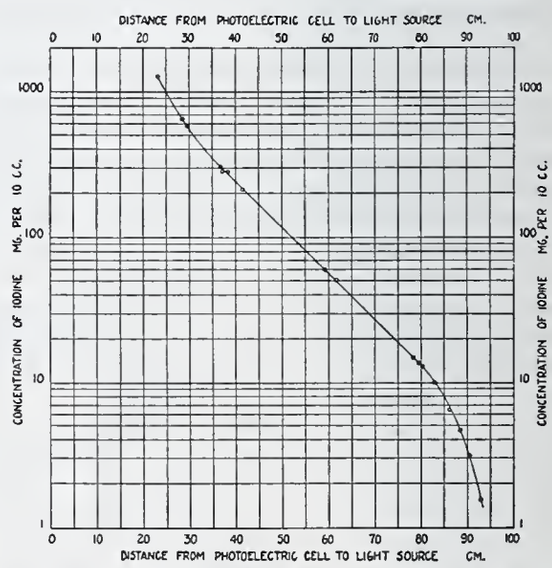

Figure 4. Calibration of Photoelectric Colorimeter with Iodine Solutions

(2:1 ratio of KI to I_2 in solution)

pure state. The strength of diluted solutions was ascertained by titration with sodium thiosulfate, according to the standard analytical method. The calibration curve for the colorimeter is shown in Figure 4.

From the shape of this calibration curve, it is apparent that the color intensities of iodine solutions cannot be proportional to iodine concentrations throughout the whole experimental

range (*1*, *2*, *3*, *5*). It is of interest, however, that for the major portion of the curve the logarithms of iodine concentrations are a straight-line function of distances to which the lamp must be moved to obtain the standard ammeter readings. Because of the questionable value of the iodine colors as indicators of the color intensities of petroleum oils, no further work along these lines has been done.

The change in the color intensity of oils on diluting them with benzene was investigated in order to determine the additive character of the proposed scale. The experimental data presented in Table III include also the Lovibond colors and the "true" colors (*4*) of the same diluted samples. The Lovibond colors were taken by several experienced operators and are given as average readings in order to obtain their best possible approximation. It is believed that the color intensities of diluted solutions obtained by means of the photoelectric colorimeter are as additive as might be expected theoretically, being superior in this respect to many other color scales now in use, but still unsatisfactory.

Table III. Colors of Lubricating Oil Solutions in Benzene

Volume of Stock in Benzene Solution	Iodine Color Intensity	Lovibond Color 500 Amber Series 0.25-in. Cell	True Color	Color Intensity
%	*Mg./10 cc.*			
1. Mid-continent cylinder stock (treated)				
100	318	360	700	405
50	116	230	350	245
25	44	150	180	130
12.5	19.2	77	83	62
6.25	9.4	38	38	28
3.125	3.8	15	15	12
2. Coastal cylinder stock (treated)				
100	122	220	325	250
50	41	120	145	125
25	16.6	59	61	52
12.5	7.8	29	29	22
6.25	3.3	15	15	10
3. Pennsylvania cylinder stock (percolated)				
100	357	350	660	425
50	113	210	305	245
25	41	120	145	125
12.5	18.3	61	63	59
6.25	9.0	34	34	26
3.125	3.7	13	13	11
4. Pennsylvania cylinder stock (percolated)				
100	22.8	112	125	74
50	12.9	64	68	38
25	6.5	40	40	19
12.5	3.4	22	22	10

In making dilutions it has been found that the same color intensities of diluted samples are obtained, irrespective of whether benzene or a "colorless" medicinal oil was used as diluent.

The proposed method for evaluating colors of lubricating oils is a means of measuring only the color intensity and does not take into consideration other attributes of color—i. e., hue and saturation. The determination of these attributes, particularly the hue of the oil, might be possible by means of the same photoelectric colorimeter but equipped with color filters. The information now available on this subject is not sufficient, however, to warrant its further discussion.

The 5.2-mm. oil cell has been used almost entirely in the development work with this colorimeter. For all oils which are darker than a bright yellow (2 NPA), a cell of this thickness is very satisfactory. As the trend is now toward lighter colored oils, the use of a thicker oil cell is desirable in order to obtain greater precision in these oils. Therefore, the use of one-inch cell and a shorter working distance (50 cm.) has been adopted for the new design. These changes do not affect the principles or operation of the instrument except that dilution of very dark oils may be required. This is considered to be justified in view of the greater precision throughout most of the scale and especially with pale yellow oils below 2 NPA.

Acknowledgment

The authors wish to thank W. V. Betts of this laboratory for making some of the measurements included in this paper.

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Device for Removing Frozen Glass Stoppers from Reagent Bottles

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An efficient stopcock key remover (*1*) has recently been described which possesses many novel and desirable features. With a small and readily available addition to this device, it may be made to serve as an excellent means for the removal of "frozen" glass stoppers from reagent bottles. The necessity for such an instrument is apparent. Its value is emphasized in the handling of bottles containing such chemicals as bromine, fuming sulfuric acid, etc.

The addition is shown in Figures 1 and 2 and consists of a U-shaped bar, *A*, which fits under the jack screw, *C*, and rests upon the outer edges of the bottle opening. The jaws (*B-B*) fit around the head of the stopper and are adjusted by the knurled nut, *D*, to accommodate stoppers of various sizes. Pressure is applied upward upon the head of the stopper by the downward force of the jack screw upon the bar, *A*. The stopper is then lifted from the bottle.

Figure 1

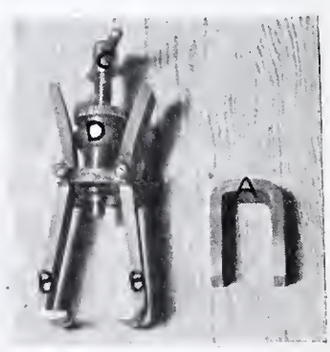

Figure 2

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The Use of the Slide Rule in Calculating Hydrogen-Ion Concentration and pH Values

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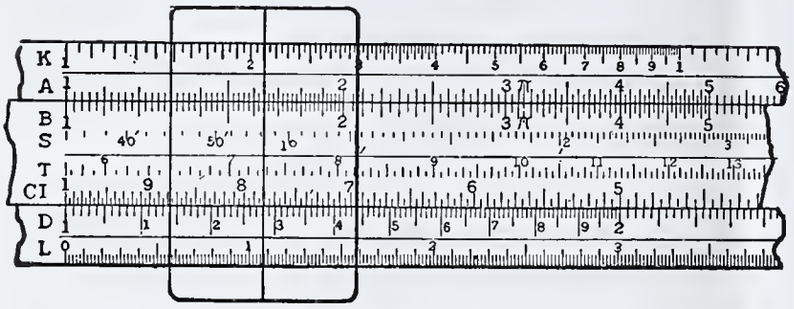

Figure 1

THE method now in use for the calculation of pH values by means of the slide rule is to set the number desired on the D scale and find the logarithm on the L scale, which involves the following calculations:

Given $(H^+) = 7.8 \times 10^{-4}$, find pH.

$$\begin{aligned} pH &= 1/\log (H^+) \\ &= 4\text{-}\log 7.8 \\ &= 4\text{-}0.892 \\ &= 3.108 \end{aligned}$$

By the method here proposed the required value may be read directly.

7.8×10^{-4} must be expressed as 0.78×10^{-3}. Then pH = 3 +. 0.78 is set on the CI scale and read directly on the L scale as 0.108. Then pH = 3.108.

Again, given $(H^+) = 3.339 \times 10^{-6}$, find pH.

Expressing the value of (H^+) as 0.3339×10^{-5}, pH = 5.477. 0.477 is read on the L scale under 78 on the CI scale.

The procedure for finding (H^+), given pH, is the reverse.

Given pH = 6.3, find (H^+).

$(H^+) = 0.5 \times 10^{-6}$. The 5 is read on the CI scale above 3 on the L scale.

Received January 24, 1933.

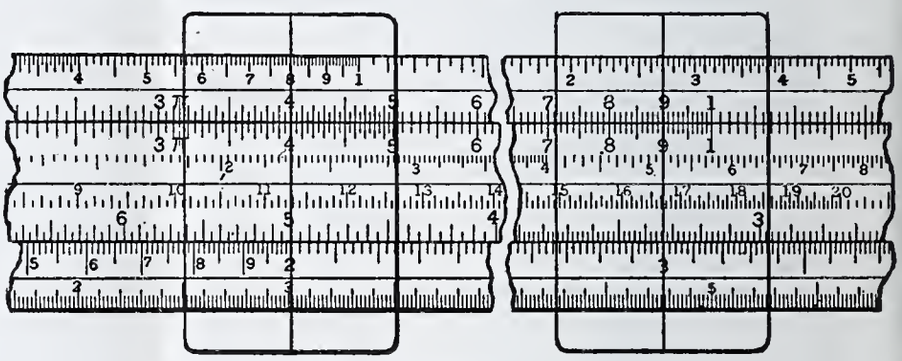

Figure 2

Improved U-Type Mercury Thermoregulator

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MUCH work on automatic temperature controls has been done to minimize the control current through the thermoregulator in order to diminish the rate of corrosion at the metal-mercury contact. This would have been unnecessary if an inert gas had been maintained at the contact. Several investigators have stressed the difficulty of providing and maintaining an inert atmosphere. A modification of the method described by Clark (*2*), which has been adapted to the ordinary U-type mercury regulator, has proved so simple and satisfactory that its description may be of value to others.

The regulator (Figure 1) is completely assembled from Pyrex glass with a tungsten wire (*5*) sealed in place at C. This wire extends about 1 cm. into the capillary which is approximately 1 mm. in diameter. The side arm, B, of the contact chamber is bent as shown and drawn down for sealing off. Clean dry mercury is then added at E until it reaches somewhat above the stopcock, which is about level with the contact point in the capillary. Dry hydrogen from a source of conveniently small pressure (Kipp generator or gasometer) is admitted to the contact chamber by means of a three-way stopcock, which permits connecting the contact chamber alternately with the hydrogen source and the air. By applying suction at E when connected with the hydrogen source and releasing when opened to the air, the chamber may be thoroughly washed out and filled with hydrogen. Finally the hydrogen is introduced until the mercury stands about 1 cm. below the wire in the capillary when the stopcock of the regulator is closed. The chamber is then connected with the air via the three-way stopcock and immediately sealed off.

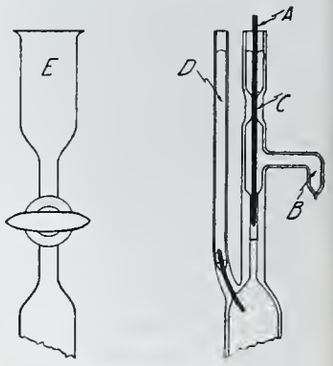

Figure 1

To set the regulator for control at a desired temperature, it is allowed to attain this temperature with the stopcock open. Then, with the circuit breaker connected at A and D (via mercury), slight suction or pressure is applied at E until the mercury barely contacts the tungsten wire, when the stopcock is closed. To change the setting to another temperature merely requires opening the stopcock and repeating the above procedure. It is thus not necessary to move the regulator in order to change the setting.

To eliminate the necessity of opening and refilling with hydrogen when too little has been left in the contact chamber to permit breaking contact by gentle suction at E (a difficulty often encountered), the side arm is bent down as shown at B. This permits trapping some of the mercury away from

the main body and thereby lowering the level of the mercury sufficiently to break contact by gentle suction. With the volume of the contact chamber approximately 1 cc., gentle suction and pressure produce a movement of the mercury surface in the capillary of about 2 cm.

Gouy (*3*) was probably the first to show that an oscillating contact gives more precise temperature control. Beaver and Beaver (*1*) obtained this oscillation by causing movement of the mercury surface rather than the wire. Such vibrations of the mercury surface have been produced in this regulator by trapping pockets of air with the mercury in the arm carrying the stopcock and supporting the regulator in such a way that the vibration of the stirring motor is imparted to it.

This regulator is used in connection with the alternating current circuit breaker, described by Ramsey and Watson (*4*), to control the temperature of water baths of approximately 100 liter capacity. With a U-tube about 30 cm. in length and 2 cm. in diameter, holding nearly 225 cc. of mercury, the maximum variation in temperature of such baths is less than 0.01° C.

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An Inexpensive Grinder

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An efficient grinder made of ordinary laboratory apparatus, illustrated in Figures 1 and 2, was designed to provide a means of breaking up bacteria without the degenerative protoplasmic changes accompanying chemical methods of disintegrating the cells. For this purpose it has been found greatly superior to the ordinary ball mill. In 6 hours this grinder crushes almost 100 per cent of the cells in 0.2 gram of dried bacteria of a very resistant species (Staphylococcus); whereas the whole cells predominate in the ball mill after 150 hours. The usefulness of this apparatus in grinding almost any nonfibrous material can be readily appreciated.

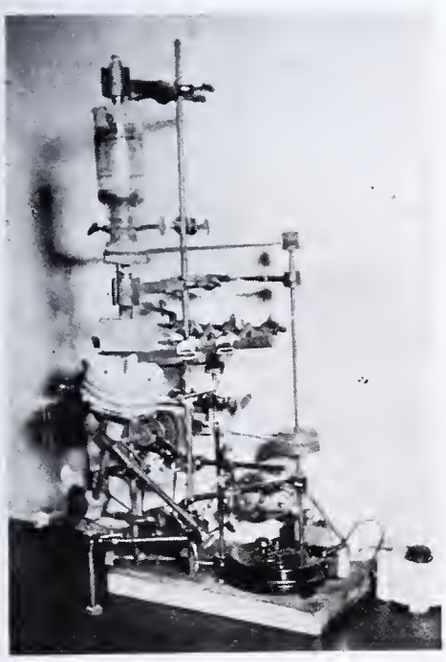

Figure 1. Set-Up of Grinder

The agate pestle and the heavy glass rod *E* are tightly fitted into holes drilled in the hardwood block *H*. The shaft *E* revolves in two bearings, each consisting of a short length of heavy-walled glass tubing *G*, and a rubber bushing *F* made by grinding the tapered portion off a rubber stopper, held by a large test-tube clamp *A*. An inverted bottle *C*, held in place by rubber stoppers *B*, serves as a receptacle for water or mercury, permitting great variation in pressure. The motive power is applied by a belt passing over the grooved rubber stopper *D*. The glass on glass bearings must of course be well greased. A more substantial type of bearing can be made of wood. A cylindrical block (a section cut from a broomstick) is drilled through the center and soaked (under reduced pressure) in oil or hot grease.

Pestle and mortar *I* revolve in the same direction, the former describing ten circles during one revolution of the latter. One of the two large corks *J* cut out to receive the mortar is grooved to take the drive belt. The corks are fastened together and to a wooden base *K* with dowels and glue, the whole being inclined about 20° to the horizontal. The table socket *L* is the type of support rod base commonly sunk flush with the table top and screwed down. It is screwed to the base *K* and serves to connect the mortar unit rigidly to a small support rod *M*. This shaft revolves in two brass bearings, each consisting of a short length cut from a cork borer *P* and a cork bushing *N*, held by a test-tube clamp *A*.

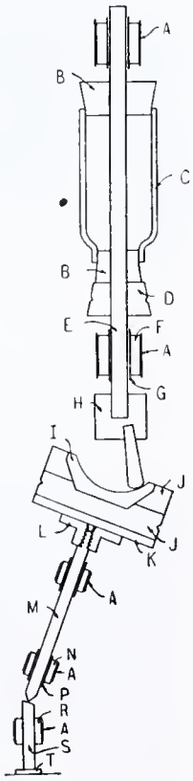

Figure 2. Diagram of Grinder

Since the weight of the whole apparatus rests on it, the bearing at the end of the inclined shaft was made of the point-plane type to reduce friction. After several months of hard use it showed little wear.

A cork *R* was slipped over the rod *S* so that it could be held firmly in place by the clamp *A*. The rubber pad *T* was placed in the position illustrated to absorb vibration produced during the grinding of some substances.

To obtain the speed reduction necessary to use a small laboratory motor, a pulley and belt system was used. The most satisfactory results were obtained with grooved rubber stoppers as pulleys and 0.125-inch (0.3-cm.) leather belting. Heavy string (chalk line) serves well as belting, but has a tendency to cut the pulleys.

Two upright rods, fastened either to a substantial base or the table top, were used to support the apparatus.

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Rapid Qualitative Detection of Mercury in Organic Compounds

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ALTHOUGH this test is especially applicable to organic mercury compounds, because these compounds, in general, do not exhibit the characteristic reactions of ionic inorganic mercury, it may be used also to detect inorganic mercury. It uses the sensitive cuprous iodide reagent suggested by Artman (*1*) in a simple volatilization tube.

A Pyrex test tube with a slotted one-hole cork is used. A glass rod passes through the cork and extends into the tube. The end of the glass rod, which is coated with the reagent, is placed about 15 mm. above the surface of the sodium carbonate mixture.

PREPARATION OF CUPROUS IODIDE REAGENT

The reagent is an aqueous suspension of cuprous iodide, prepared by mixing finely powdered cuprous iodide with about an equal weight of distilled water. If the cuprous iodide is not at hand, it may be conveniently prepared by the following procedure from common laboratory chemicals:

Solution 1. Copper sulfate, 5 grams; water, 75 cc.
Solution 2. Sodium sulfite, 5 grams; potassium iodide, 11 grams; water, 75 cc.
Dissolve solutions 1 and 2 separately, then mix and allow precipitate to settle. Filter or centrifuge and wash with water.

PROCEDURE

Mix about 5 to 10 mg. of the organic compound to be tested with about 0.5 gram of anhydrous sodium carbonate and place in a dry test tube. Dip the glass rod to a depth of 4 to 5 mm. into the cuprous iodide suspension, remove, and allow to dry partially. Place the coated rod in the test tube. Hold the tube at a 45° angle and heat the lower end gently with a small flame. In the presence of mercury, the reagent quickly turns from white to a salmon color or pink. The reaction is very sensitive, the limit using this procedure being about 0.02 mg. of mercury.

Too prolonged heating of the fusion mixture is unnecessary and is to be avoided, as the application of a high temperature decomposes the reagent.

Arsenic and antimony do not interfere. Organic substances containing nitrogen, which give off ammoniacal or other alkaline vapors on decomposition with sodium carbonate, interfere with the test by reacting with the reagent. However, this can be circumvented by carefully placing a 2-mm. layer of potassium pyrosulfate over the alkaline fusion mixture. This will absorb the alkaline vapors during heating and not affect the sensitivity of the test.

Compounds containing sulfur in certain linkages also interfere by generating sulfide vapors which change the color of the reagent to black. This interference can be prevented without loss in sensitivity by carefully placing a 2-mm. layer of lead oxide (litharge) over the sodium carbonate mixture.

Reliable and rapid results were obtained by the use of this test on a host of mercury compounds. It was also successfully applied to the detection of mercury in soaps, antiseptics, and ointments. In these cases it was necessary to use a sample that would give about 1 to 2 mg. of mercury and increase the amount of sodium carbonate used. The test as described is not recommended for toxicological detection of mercury because of the large size of sample necessary and the difficulty of completely absorbing the large volume of ammoniacal vapors developed on heating the protein material.

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Nickel Tubes in Organic Combustions

FRANCIS EARL RAY, University of Cincinnati, Cincinnati, Ohio

IN A RECENT article Couch (*2*) reports an interesting method for the analysis of difficultly combustible organic compounds. The author encountered similar difficulties in the combustion of nitro compounds of high molecular weight. The material would volatilize and condense as a tar on the glass tube and could not be properly burned. When nickel tubes (furnished through the courtesy of C. J. Bianowicz of the International Nickel Company) were substituted for glass, the material could be burned completely.

Certain nitro and nitroso compounds, however, gave high values for nitrogen when burned in a metal tube and nitric oxide was found in the nitrometer unless the combustion was carried out with tedious slowness. Evidently the reduced copper spiral was not very effective, possibly because of the completely oxidized interior of the tube. This difficulty was surmounted by mixing the sample in a porcelain boat with copper powder (Karlbaum's Natur-Kupfer). The results obtained by this method were very satisfactory.

In using a nickel tube, 12-inch (30-cm.) lengths of 0.125-inch (0.3-cm.) copper tubing were wound around the combustion tube at each end and a stream of water was passed through these coils to prevent the rubber stoppers from melting. A nickel tube open at both ends was used. Carbon dioxide was generated in a small Kipp from marble chips previously boiled with slightly acidulated water. If the closed-end Dumas tube is preferred, one end of the nickel tube may be threaded and a threaded nickel cap screwed firmly in place.

Nickel tubes have also given excellent service in carbon-hydrogen combustions.

A nickel tube is good for at least one hundred combustions for carbon and hydrogen or a much greater number of nitrogen determinations. The combustions may be carried out rapidly as the tubes may be cooled between heatings with a blast of air. The tubes are not, of course, brittle, which is the objection to silica tubes, nor do they oxidize rapidly and quickly deteriorate as do copper tubes (*1*, *3*).

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HARRISON E. HOWE, EDITOR

The Chemical Analysis of Things as They Are

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AT THE outset we might ask the question "Why are chemical analyses made?" The crude analyses of the earliest days were the explorations in an unknown world, the charting of naturally occurring materials and of the simple compounds that were then made by man. Next came the analyses upon which the present structure of chemistry, geology, and many of the other sciences is based. Those were the happy days in which most research workers made their own analyses, and the profession was in high standing. Today, by far the greater number of chemical analyses deal with materials that enter into commerce, man-made materials for the most part, in which man has outdone his Maker. Moreover, these analyses are usually made by second or third parties who are often entirely divorced from the history of the material or the purpose of the analysis, and who therefore are not only working in the dark but also often have only a monetary interest in the test. The need and importance of chemical analyses are not dying out, for chemical analysis now serves the arts as well as the sciences. It therefore seems appropriate to record some observations on present trends, and on considerations that should not be overlooked.

"The Chemical Analysis of Things as They Are" has been chosen as a subject because so many talks and articles on analytical subjects deal with "The Chemical Analysis of Things as They Are Not." This has been brought about because in the field of analytical chemistry, as in other fields of endeavor, there has been a constant drifting toward specialization. As a consequence, there is an increasing tendency to devote more and more time to determinations which deal with the final act of a chemical analysis, and less and less time to chemical analysis itself—in other words, to consider chemical analysis as dealing with one or two variables instead of the dozen or more that are often involved. This gradual loss of the analytical viewpoint is evident in contemporary articles that purport to deal with chemical analysis.

For example, in a recent article entitled "Determination of Aluminum" it is claimed that good determinations of aluminum can be had by adding lithium chloride, treating with ammonium hydroxide until phenolphthalein turns pink, filtering, washing, igniting, and weighing as the compound $5Al_2O_3 \cdot 2Li_2O$. Not one word is said concerning the behavior of the other elements. To the analyst, it is self-evident that approximately one-half of the elements can be precipitated under these conditions. His chief thoughts on encountering such a reaction would therefore not concern its use for the determination of aluminum, but rather what effect lithium would have on determinations of aluminum and iron that are made by precipitating with ammonium hydroxide in the usual manner, and whether aluminum causes retention of lithium in methods for separating lithium from accompanying elements.

Methods of the type described are about as helpful to the analyst as the method for catching a bird which the old folks used to recommend to children—namely, to sprinkle salt on its tail. To do that, one obviously must have the bird in hand, and in that case there is no need for the salt. So it is with much of the advice that the analyst receives. Minute directions are given for the salting away of the quarry after it has been separated from its fellows. In this connection, it is interesting to note that when the analyst does happen to encounter a "pure" compound his chief concern is with the impurities rather than the major constituent. In other words, the absolute purity of a pure compound is established by determinations of its impurities.

A contributing factor to the state of affairs that has been outlined was the decision some years back that the analyst was a benighted creature who was working in the dark and sadly in need of enlightenment. And so the structure of analytical chemistry was brought under the spotlight, usually by nonanalysts. Appropriately, the "foundations of analytical chemistry" received first attention. Without question, a study of the foundations of analytical chemistry is eminently fit and proper, provided one finally leaves the cellar. But too many never attempt to reach the upper floors, and so their outlook is restricted and their viewpoint narrow. And they never know the delights of browsing in the attic, and dusting off some of the old antiques that should either be renovated or discarded—heirlooms like the methods for silica and for alumina—not to mention many others.

Of course there is a good reason for confining analytical discussions to determinations which involve one or two variables. A system containing ten to twenty diverse components can hardly be handled on a strictly scientific basis, and any handling of it requires actual experience in analysis. The solubility product of hydrated aluminum

oxide can be brought into the picture if ammonium hydroxide is added to a solution of pure aluminum sulfate. But what about precipitations that are made in a solution containing iron, titanium, phosphorus, vanadium, and a dozen other constituents as well? The difference between the two problems is illustrated in Table I. The first case, that of aluminum sulfate, represents chemical analysis as it is not. The second, that of bauxite, represents chemical analysis as it is, and is no exaggeration, for thousands of tons of bauxite are sold, and naturally one of the most important considerations in the sale is the alumina content. If aluminum sulfate is pure enough to warrant precipitation by ammonium hydroxide, followed by filtration, ignition, and weighing of the resultant Al_2O_3, the operations are a waste of time, for one would get the same result much more quickly by igniting the weighed sample and then again weighing. In the case of bauxite, treatment with ammonium hydroxide yields all of the first eight constituents and more or less of the copper. Obviously then, the analysis resolves itself, not to a simple determination of aluminum, but to a complex analysis in which, as a matter of fact, the aluminum ion is never precipitated by itself.

Table I. Determination of Aluminum

Material	Components							
$Al_2(SO_4)_3.18H_2O$	Al_2O_3	SO_3	H_2O					
Bauxite	Al_2O_3	Fe_2O_3	TiO_2	ZrO_2	P_2O_5	V_2O_3	Cr_2O_3	SiO_2
	CuO	MnO	CaO	MgO	Na_2O	K_2O	SO_3	H_2O

So we have two classes of workers in the analytical field, the determinators and the analysts. The determinators, who are by far the more numerous, may in turn be divided into two general classes: first, the common determinators who follow a method explicitly, without knowledge or concern as to the reactions involved; and second, the educated determinators who can handle systems containing one or perhaps two variables, or who, like determinators of pH, are chiefly interested in group effects and make no effort to go beyond this. The first are the laborers. They need not be chemists, and they require constant supervision. The second are the white-collar workers who exhibit the usual extremes of workers in this classification. The determinator's salvation lies in the development of truly selective methods of analysis, and his final resting place will be a heaven in which he has a shelf containing 92 reagents, one for each element, where No. 13 is the infallible specific for aluminum, No. 26 the sure shot for iron, No. 39 the unfailing relief for yttrium, and so on to uranium.

As for the analyst, he is a comparatively rare bird and is often referred to as a disappearing species, like the old family practitioner who does the best he can, guided by theory and experience, of which the most comforting is experience. It must be admitted that one of the reasons for the gradual disappearance of the analyst is the anomaly that, in spite of the fact that he works entirely with material things, his reward is chiefly spiritual. Who ever heard of a consulting analyst, or of an analyst who patented a new method of analysis or incorporated a company to promote its use? Other reasons for the scarcity of analysts are perhaps the peculiar characteristics, some inherent and some acquired, that he must possess. He must have the inquisitive habit of a detective, for oftentimes the composition of the material under test is absolutely unknown. He must be an expert manufacturer of pure chemicals, for on this ability the success of his gravimetric determinations depends. He must be an efficient dispenser of liquids of which he knows the exact effect. And, above all, he must serve a long apprenticeship, and keep in constant practice.

So much for the personnel and the general aspects of the project. We come now to the most important details of the job. These are (1) the sample on which the analysis is made, (2) the method of analysis that is used, (3) the accuracy of the result, and (4) the cost of the analysis.

The Sample on Which the Analysis Is Made

Most analysts are well aware of the difficulties that attend the taking of a truly representative sample of the material that is to be analyzed. Not so well understood are the pitfalls in the way of obtaining the smaller sample on which the analysis is actually made, pitfalls such as (1) differences between the compositions of fine and coarse particles; (2) the fixation of oxygen, water, or carbon dioxide during grinding, sieving, or drying; (3) uncertainties as to the water content after drying and weighing the sample; and (4) changes in the composition of the sample during storage. The extent of errors that may be caused by the first and last are illustrated in Tables II and III.

Table II. Differences between the Compositions of Particles in a Sample

Material	Sieve Size	Composition		
		Carbon		
Cast iron	14–20	2.45		
	20–30	2.27		
	30–40	2.04		
		Copper	Lead	Tin
Journal bearing	14–20	70.0	24.4	4.9
	20–30	70.2	24.1	4.9
	30–80	67.6	27.9	4.7
	>80	63.2	31.2	4.4
		Tungsten		
Ferrotungsten	80–100	77.6		
	100–200	80.2		
	200–325	79.5		
	>325	70.4		

Table III. Changes in Samples during Storage

Material	Composition When Prepared	Composition after Storage
	%	%
Ferrovanadium	33.6 V	33.1 V
Zinc ore	31.4 Zn	30.4 Zn
Soda-lime glass	74.1 SiO_2	73.4 SiO_2

For examples of errors that may be caused by oxidation, we have but to turn to examples such as the oxide film formed on the particles obtained in machining samples of steel that are to be used in determinations of oxides in steel, the oxidation of sulfur in samples of pyrite that are ground instead of crushed, or the more insidious oxidation of sulfide ores such as sphalerite that takes place during drying or storage. With regard to the fixation of water and carbon dioxide, it is interesting to note that many fired materials and not a few rocks exhibit this property, particularly when in the finely powdered state. For example, samples of a soda-lime glass which had been dried at 105° to 110° C. showed no loss on ignition in the solid state, 0.5 per cent when first ground and sieved, and 1.0 per cent a few years later, even though it had been stored in a can with a fairly close cover. Hydrated materials present special problems, especially if they are to be used as standard samples, for the expulsion of water may be so gradual that portions of the same material dried for like periods at 105° to 110° C. retain quite different amounts of water. Finally comes the old question of hygroscopicity, which presents no mean problem at times. Pyrolusite, for example, while not markedly hygroscopic, is sufficiently so to cause entirely erroneous results if two successive samples are taken from the same dried portion. It may be remarked that difficulties in sampling are not confined to commercial materials. Many an analysis of a "mineral" is useless and misleading for lack of care in selecting the sample, and many a determination of atomic weights has been in error because the sample on which it was made was not worthy of the analytical effort that was put on it.

Table IV. First Results Reported in Coöperative Analyses of Argillaceous Limestone

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	MnO	CaO	MgO	Na_2O	K_2O	S	CO_2	Loss on Ignition
	13.55	3.35	0.53	0.11	0.08	0.03	41.00	2.06	0.21	0.62	0.18	33.36	34.40
	13.87	3.91	1.31	0.16[a]	0.11	0.036[a]	41.23[a]	2.07	0.28	0.62	0.20	33.51	34.45
	13.90	3.93	1.57[a]	0.17	0.14[a]	0.04	41.23	2.10	0.29	0.69[a]	0.23	33.65[a]	34.49
	13.98	4.08	1.63	0.18	0.15	0.044	41.24	2.15	0.38	0.74	0.24[a]	34.12	34.53[a]
	14.02	4.17[a]	1.65	0.22	0.16	0.06	41.42	2.17[a]	0.39	0.74	0.27	...	34.54
	14.03	4.23	1.66	0.25	0.18	0.06	41.58	2.22	0.41	0.76	0.28	...	34.56
	14.12[a]	4.30	1.67	0.32	0.20	0.12	41.62	2.23	0.43[a]	0.77	0.29	...	34.60
	14.12	4.30	1.73	0.34	0.44	...	41.64	2.24	0.45	0.82	0.31	...	34.69
	14.18	4.68	1.77	..	..	...	42.20	2.26	..	..	0.32	...	35.10
	14.30	4.89	1.78	..	..	...	42.38	2.40	..	..	...	...	...
						AVERAGE DEVIATIONS FROM MOST PROBABLE VALUES							
1930	0.161	0.296	0.22	0.071	0.065	0.021	0.37	0.08	0.08	0.065	0.042	0.225	0.121
1905	0.19	0.25	0.11	0.02	0.02	0.04	0.24	0.13	0.19	0.04	0.02	0.17	...
						AVERAGE PERCENTAGE ERRORS IN 1930							
	1	7	14[b]	44	46	59	1	4	19	9	18	0.6	0.4

[a] Result nearest to the most probable value.
[b] 8 if the result 0.53 is omitted.

Method of Analysis

The second consideration in the chemical analysis of everyday materials is the method of analysis that is used. It is evident that the method should give the result that is desired. It is not so well understood that all methods of chemical determination are in reality based on reactions of groups, and that they can give accurate results for a given member of the group only so long as the other members of the group are absent or their effects can be discounted. Thus, determinations of the chloride ion by precipitation as silver chloride succeed, provided ions such as bromide, iodide, monovalent thallium, or lead are absent; determinations of iron by reduction with zinc and titration with permanganate leave little to be desired, provided the solution is free from elements such as titanium, chromium, vanadium, or molybdenum; and the electrodeposition of copper is almost perfect unless attempted in the presence of elements such as bismuth, antimony, mercury, silver, gold, or tellurium. Moreover, many do not seem to appreciate that an element in the presence of others may behave quite differently than when it is by itself.

There is no dearth of methods that are entirely satisfactory for the determination of elements when they occur alone. The rub comes in because elements never occur alone, for nature and man both frown on celibacy. Methods of determination must therefore be judged by their "selectiveness." It is in this respect that most methods are weak and that improvements must come, improvements such as are shown in the recently discovered α-benzoin oxime method, which not only provides a separation of molybdenum from practically all the elements, but also yields a precipitate that can be used for its quantitative determination as well. Think what a boon the discovery of a simple, selective precipitation procedure for the determination of silica would be. Or simple direct methods for the determination of everyday elements such as aluminum, calcium, magnesium, sodium, and potassium, or important commercially used elements like antimony, cobalt, beryllium, boron, and tantalum.

We are also in need of more simple and accurate methods for the determination of substances that are present in very small amount. Most of the present-day methods require entirely too much time, and results are none too satisfactory. It is not uncommon for two determinators to report results which differ by as much as 500 per cent. Such errors are not confined to chemical analysis alone. They apply equally well to estimations made by physical methods, such as spectroscopic, the only difference being that they are not so well known. It might be observed in passing that spectroscopic tests of things as they are are by no means infallible. The term "spectroscopically pure" has a quantitative limitation which is sometimes much more serious than is suspected. In quite a few applications, the spectroscope is not so sensitive as chemical methods. For example, the chemist can easily discover amounts of molybdenum or antimony in steel, or bismuth in copper that the spectroscopist cannot detect by direct test. The spectroscopist can, however, always excel the chemist by combining spectroscopy with chemical analysis—in other words, by first making separations in which the element that is sought is separated from most of the accompanying elements, and then properly concentrated before the spectroscopic test is attempted. The sensitivity of such tests is bounded only by the analyst's ability to control his blanks.

Because of their lack of selectivity, methods for the chemical analysis of things as they are do not stay put. Therein lies the danger of standard methods of analysis. As soon as the other group members creep in—for example, through changes in manufacture—the method must be changed. We cannot determine tin in steels by the same method that is used for tin in bronzes, not because of the presence of the larger amounts of iron, but because steels are prone to carry group members such as molybdenum and vanadium, whereas bronzes do not—as yet. The most excellent bismuthate method which we use for a plain carbon steel must be discarded when we encounter a steel containing cobalt; the standard procedure for carbon in steel was entirely satisfactory until special steels such as those of the high-sulfur or 18-8 types were made; the evolution method for sulfur in steels fails with those containing titanium, zirconium, or selenium; and the methods for silica and alumina in glasses begin to waver when boron is encountered.

One criticism of present-day researchers in analytical chemistry is that there are too many repairmen as compared with builders. In other words, too many are tinkering on old methods of determination that are scarcely worth the attention, as compared with pioneers who blaze new trails. We have gone about as far as we can go along the old paths. Worthwhile developments must come as a result of new methods of attack, such as the utilization of complex ions, or a systematic study of the reactions of organic compounds.

How far we have advanced in the chemical analysis of things as they are during the past 25 years can be illustrated by the data shown in Table IV.

As for newly proposed methods of analysis, it might be pleaded that the author (1) tell in what respects the method is superior to established methods, including considerations such as time required and accuracy of results; (2) enumerate the substances that prevent its use; (3) outline its desirable applications; and (4) tell the whole story in one installment, or at least give a good synopsis of the whole story in the first installment. There is no excuse for passing out information in the "continued in our next" style, which, for example, characterized articles on the use of 8-hydroxyquinoline.

Accuracy of the Result

We have now arrived at the third consideration in the chemical analysis of things as they are—namely, the accuracy of the result obtained. There is a wide misconception, even among analysts themselves, as to the accuracy of the results obtained in analytical work, and many confuse precision with accuracy. It is a comparatively simple matter to establish the precision that can be expected if a certain method of analysis is applied by an analyst or by a group of analysts to a given material. On the other hand, it may be extremely difficult to judge the probable accuracy of a result, for all results are matters of opinion rather than fact, and so the true result is never known. This is one of the most unsatisfactory aspects of chemical analysis. When an analyst scans a bare result, he can never be sure whether the determinator provided for all interfering compounds, hoped that they were absent, or was too ignorant to worry. How difficult the task may be can be illustrated by the data shown in Table V. These represent the results that were reported by thirty different analysts situated here and abroad. It can be seen that 60 per cent of the analysts reported results that were essentially within the average deviation from the general average, and that the average deviation (precision that can be expected if the same analysts determine calcium phosphate in this type of material) is in the neighborhood of 0.33 per cent. But what about the most probable value? Is it the general average, is it within ±0.33 of the general average, or is it a value outside of this limit? Anyone who chose the result (77.40) that shows the greatest deviation from the general average would be regarded as taking a very long shot, and yet this is the one which is nearest the correct result. That such difficulties are not confined to everyday analyses is illustrated by the history of the atomic weight of antimony. This was given as 120.062 ± 0.0037 by Clarke in 1920, after most carefully reviewing and weighting the determinations of the atomic weight of antimony that had been made up to that time. He states that "the figure is not quite satisfactory" and "that some more work should be done." Subsequent analyses bore this out, for 120.2 was adopted in 1921, and the still higher weight 121.77 was chosen in 1925. Note now that this weight is not very far off from the value 121.82 which Clarke obtained by recalculating analyses made by Dumas in 1859, and of which Clarke stated "The values, say all over 121, are almost certainly in error, and ought to be rejected."

Table V. Analysis of Phosphate Rock

(All analyses on dry basis)

$Ca_3(PO_4)_2$ Reported by Thirty Laboratories throughout the World				
%	%	%	%	%
77.40	78.07	78.33	78.61	78.77
77.73	78.16	78.33	78.62	78.79
77.77	78.19	78.40	78.62	78.81
77.84	78.21	78.42	78.63	78.84
77.85	78.24	78.42	78.72	78.86
77.96	78.28	78.60	78.72	79.10

General average, 78.38
Average deviation from general average, 0.33 (14 low and 16 high)

A fair question therefore is: "How can the most probable value be established?" In classical researches, as in determinations of atomic weights, it is chosen by most carefully examining the credentials of the candidate. These must be in minute detail and, in the case of atomic weights, would suffice except for one serious omission, the integrity of the sample, for which no one on earth can vouch. In the analyses of everyday things, the safeguards that attend the acceptance of atomic weights are of course impossible, because cost and time are prohibitive. When arguments arise, industries usually employ an umpire, who often knows less about the game than the disputants, or the results are checked against a standard sample of like composition. How the most probable value is established for standard samples, such as are furnished by the Bureau of Standards, is a long story that can be summarized by the statement that it is based on experience, on the work of others in the field, and usually on determinations made by as many fundamentally different methods as possible.

As for estimating the accuracy of his work, it can be said that the determinator is usually an optimist in thought and expression, while the analyst is a confirmed pessimist. The determinator reports silica in glass as 71.61, if not 71.611. The analyst, who knows that he is doing nicely to insure results in the first decimal place, reports 71.6 and thus is honest with himself and deceives no one as to his powers. The percentage errors that have been made by representative analysts who have done the best they could in analyses of materials with which they were familiar are shown in Tables VI and VII and emphasize the fact that the ordinary analyst of things as they are is not so much concerned with keeping his errors below one part in one thousand as he is in keeping them below one in one hundred. It should be observed that the accuracy is high in determinations of the high-priced constituents, and that, while the accuracy is not flattering in many of the other determinations, it is still inside the limit at which the data can be used. Moreover, in most cases the accuracy in terms of the material is quite satisfactory. As regards the correlation of data, an error of one point (0.01 per cent) in determinations of carbon in a 20-point (0.20 per cent) carbon steel represents a 5 per cent error, and is yet within the accuracy of ordinary sampling and any use that can be made of the analysis in the ordinary case. With respect to accuracy in terms of the material, we may easily report 0.051 per cent for sulfur in a steel containing 0.050 per cent. This error in terms of the steel is but 1 part in 100,000, or equivalent to measuring a mile to an accuracy of about 0.5 inch, and it has no more significance to the metallurgist at present than the 0.5 inch has to a mile runner, or the time that is recorded. It is also obvious that even larger errors may not be fatal, provided approximately the same error is always made. For example, no harm is done if a glass batch containing 70 per cent of SiO_2 shows 65 per cent by a method that gives very uniform results and is in daily use in checking its composition. If the actual content is of moment, and the approximate error of a cheap, rapid method is known, the latter is often used and the correction made, as is done in evolution sulfurs on cast iron.

Table VI. First Reports of Analysis of Chrome Ore

Cr_2O_3	Al_2O_3	FeO	MgO	SiO_2	TiO_2	CaO	MnO
36.62	17.15	14.18	15.95	7.82	0.91	0.32	0.19
36.62	19.37	14.24	15.99	7.86	0.91	0.38	0.22[a]
36.86	20.28	14.25	16.19	7.99	0.93[a]	0.44	0.23
36.91	20.55	14.35	16.21	8.05	0.93	0.49	0.35
36.93	20.68	14.36	16.33[a]	8.21	0.93	0.58	..
36.98[a]	20.82	14.40[a]	16.36	8.22	0.98	0.68	..
36.99	20.84	14.49	16.80	8.24	0.99	0.83[a]	..
37.05	20.84[a]	14.50	17.49	8.25[a]	1.06	1.12	..
37.05	20.86	14.56	...	8.28	1.12	1.69	..
37.37	...	14.82	...	8.59	..	..	..
General averages							
36.94	20.15	14.42	16.42	8.15	0.97	0.73	0.25
Average deviations from general averages							
0.15	0.84	0.14	0.37	0.18	0.06	0.33	0.05
Averages of results that fall within average deviations							
36.97	20.53	14.44	16.25	8.21	0.95	0.60	0.23
Results outside average deviations							
3	1	4	4	4	4	4	2

[a] Result nearest to most probable value.

Cost of Chemical Analyses

When we enter the field of chemical analyses of things as they are, we step from the academic into the commercial domain, and so it is proper to discuss costs.

In this field, accuracy and costs usually go hand in hand.

Table VII. Average Percentage Errors of Determinations of Constituents of Representative Materials

Constituent	Material	Constituent %	Average Percentage Error
Si	Plain steel	0.39	0.86
Si	Tungsten steel	0.48	2.6
Si	Ferrosilicon	75.6	0.2
SiO_2	Glass	74.1	0.2
Al_2O_3	Glass	0.33	14.2
	Limestone	4.16	1.8
	Flint clay	38.77	0.45
	Bauxite	55.0	0.08
Fe_2O_3	Soda-lime glass	0.06	9.5
Fe	Manganese bronze	1.13	1.7
Fe_2O_3	Plastic clay	2.05	1.4
Fe	Hematite	68.60	0.05
C	Cast iron	2.69	1.4
	B. O. H. steel	1.01	0.8
S	A. O. H. steel	0.037	3.4
SO_3	Glass	0.41	5.1
Mn	Manganese bronze	1.59	1.4
	Ferromanganese	80.67	0.13
P	A. O. H. steel	0.037	2.7
	Ferrophosphorus	26.2	0.23
Cr	Cast iron	0.011	0.15
	Ferrochromium	67.9	0.12
Ni	Nickel steel	3.48	0.34
	18–8 steel	8.45	0.3
CaO	Lead barium glass	0.21	8.8
	Burned magnesite	3.36	1.0
	Argillaceous limestone	41.23	0.28
Mg	Zinc-base die casting alloy	0.10	5.3
MgO	Chrome ore	16.30	0.43
MgO	Burned magnesite	85.64	0.06
Na_2O	Plastic clay	0.27	18.8
	Soda-lime glass	16.65	1.7
K_2O	Silica brick	0.29	4.7
	Lead barium glass	8.38	0.96
W	High-speed steel	18.25	0.32
Zn	Brass	27.09	0.19
V	High-speed steel	0.970	0.7
	Ferrovanadium	31.15	0.36
Mo	Nitriding steel	0.163	2.5
	Calcium molybdate	35.3	0.16
Cu	Cast iron	0.151	5.4
	Phosphor bronze	78.05	0.03
Pb	Manganese bronze	0.56	3.1
	Lead-base bearing metal	78.87	0.07
Sn	Lead-base bearing metal	10.91	0.53
	Phosphor bronze	9.91	0.33
Sb	Cast bronze	0.16	10.4
	Tin-base bearing metal	7.33	0.81

So naturally the money that is spent on analyses should not exceed what is necessary to insure the accuracy that is needed. For this reason, in applied analyses we often employ two sets of methods, the cheap routine methods which we use whenever we can, and the expensive umpire or referee methods which we use only when necessary. For example, in determinations of phosphorus in plain carbon steels the rapid alkalimetric method serves entirely satisfactorily for all ordinary purposes, and so the slower and more expensive molybdate-magnesia method is brought out only in cases of serious disputes, or occasional checking of the alkalimetric method.

In any discussion of costs of analyses one should consider the producer as well as the consumer of chemical analyses. If the consumer is at the same time the producer, as in steel works or research laboratories, the situation takes care of itself, for it's all in the family. Consequently, the cost of personnel and of the methods of analysis is, or should be, that which will give the necessary results. In this case, the ratio of analysts to the less expensive determinators depends on the type of work, the former predominating in research laboratories and the latter in plant laboratories. Methods of analysis are also carefully chosen on the basis of speed, dependability, and cost.

Purchasers of chemical analyses, like other buyers, usually get what they pay for, and as a rule are unwilling to pay very much. In purchases of clothing one can buy ready-made or custom-made suits. The former are relatively cheap, because they can be made in quantity from a standard pattern, and are quite satisfactory for the man whose figure follows conventional lines. Similarly, in purchases of chemical analyses we can buy ready-made or custom-made analyses. The former are cheaper, for, like carbon in plain carbon steels, they can be made by a standard operation. They are also perfectly satisfactory, so long as the composition of the material is not unusual and ordinary accuracy suffices. The moment, however, that you depart from these specifications and enter the custom-made department, costs mount rapidly.

This leaves the producer of analyses—which is no new situation, for he usually gets left. It can be stated at the start that he seldom receives a fair return, except possibly in the case of commercial laboratories which sell ready-made determinations in large volume. Under present conditions there is little profit in custom-made analyses. One reason for this state of affairs is that the analyst sells an intangible commodity, an opinion. Under the circumstances, the purchaser cannot see why he should pay five dollars if someone else is quoting fifty cents. This might not trouble the analyst if the opinion were the result of exclusively mental processes, such as an opinion at law, for then the analyst would not be bothered much by overhead, except when talking through his hat. The difficulty is that the opinion must be based on physical as well as mental effort, and if one discounts the mental, he still has to take care of the physical. It should also be remarked that the purchaser cannot check the correctness of the opinion except by buying other opinions, which is an expensive as well as a poor way to settle an argument.

The intention in this article has been to present a picture of the chemical analysis of things as they are, and not to glorify the analyst on the one hand or to depreciate the state of analytical chemistry on the other. The work of and the demands on the analytical chemist are growing more exacting every day, and we cannot afford to lose the analytical viewpoint.

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Graphical Representation of Mineral Components in Water Analyses

In the article under the above title [(Ind. Eng. Chem., Anal. Ed., 4, 405 (1932)], no attempt was made to give an exhaustive list of authors of all the graphical systems previously proposed for representing water analyses, or to present a survey of all previous systems. However, mention might well have been made of the article by E. Herrero Ducloux, entitled, "Representación gráfica de la composición quimica de las aguas naturales," which appeared in *Physis* (*Revista de la Sociedad Argentina de Ciencias Naturales*), III, 545–9 (1918).

A. Adler Hirsch

Quantitative Analysis by Spectroscopic Methods

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Spectroscopic methods for estimating the amounts of various elements present in a mixture, alloy, or solution are reviewed and the continued advance in the precision of the determinations is noted. Further increase in precision has been attained by the authors, by making use of methods recently developed for measuring the intensities of spectral lines, and by a simple means of standardizing the arc source used in the analysis of metallic alloys. The necessity for putting an intensity calibration pattern on each photographic plate in order to insure uniformity and high precision of measurement is emphasized. The procedure adopted by the authors in making analyses of metallic alloys is described.

The value of the spectroscope in identifying substances and in detecting the presence of small amounts of certain elements in mixtures and compounds has long been recognized. The development of methods of estimating the quantity of a given element present dates from 1874, when Lockyer (*10*) noted that the spectral lines of the more abundant elements present in the electrodes of an arc can be observed farthest from the electrodes. The development of the method of persistent lines or "raies ultimes" was begun by Hartley (*8*) in 1882 and extended and perfected by Pollock and Leonard (*13*) and by de Gramont (*5, 6*). This method never proved completely successful on account of the impossibility of determining just when a line disappears from the spectrum, especially since this depends as much on the characteristics of the photographic plate and apparatus used and on the duration of exposure as upon the abundance of the test element. On account of this difficulty more recent investigators (*4, 11, 18*) turned to methods which involve the comparison of the relative strengths of spectral lines, but these also proved to be of insufficient reliability, because of the impossibility of standardizing the conditions of exposure and development of the plate over the general range of analysis.

Perhaps the greatest errors in the older methods of analysis came from the comparison of lines in different spectrograms. It is practically impossible to make equivalent exposures for the recording of spectra. Realizing this, Gerlach (*3*) developed a method of "internal control" in which the analysis was based upon finding pairs of selected lines of equal strength —one of the element under test and one of the principal or basic element in the material being analyzed. These pairs of lines are examined in the spectrum of the unknown, and analysis is made by comparison with their relative strengths in a prepared series of specimens. If no pairs have equal strength in the spectrum of the unknown, an estimate of the concentration of the test element is made by an interpolation between the steps in the standard series.

Photographic Spectral Photometry

In the foregoing discussion, the term "strength" of a spectral line has been used, without definition, to mean the relative blackness or opaqueness of the line as it appears in the photographed spectrum. The strengths of spectral lines have usually been estimated merely by examining the photographed spectrum, often during the time of measurement of the plate with a comparator. Purely arbitrary scales were chosen and the value given any line came from the exercise of the best judgment of the observer.

In making use of spectral lines in quantitative analysis, it is the intensity of the light in a given spectral line (of a given frequency) with which we are concerned and not the photographed image. The intensity of the light in the source may be expected to depend upon the amount of the element in the source that is giving forth that light. However, all we have to work with conveniently is the photographed spectrum, and we must determine from it the relative intensities of the light of different wave lengths. Accurate quantitative analysis demands the use of the best available technic of modern spectral photometry (*17*) and a full understanding of the photographic processes (*14*).

In order to provide a means of interpolating between the fixed percentages in the method of Gerlach and Schweitzer at which certain pairs of lines are equally strong, Scheibe and Neuhäusser (*16*) introduced the use of a rotating logarithmic sectored disk. The proper method for the use of this disk was pointed out by Twyman and Simeon (*21*) and used by Twyman and Hitchen (*19, 20*) in the methods of quantitative analysis developed at the Hilger laboratories.

The principal objections to the use of the logarithmic disk are the assumption of the validity of the reciprocity law, the introduction of the intermittency effect (*2*), and the difficulty in determining the exact lengths of the photographed lines. The reciprocity law is known not to be valid, and errors arising from its failure become very large in certain spectral regions. Lines photographed with a sectored disk have no definite length but gradually fade out at one end.

Like Twyman and Hitchen, Nitchie and Standen (*12*) make use of a working curve from which the amount of the test element present can be read off directly. A microphotometer is employed to measure the densities of the spectral lines, though, apparently, the blackenings were actually used in the analysis. No means of calibrating the plate is mentioned, but the authors state that only those spectrograms should be used in which the relative densities fall upon the straight-line part of the characteristic curve for the plate. With this assumption, the difference in the blackening of two selected lines is taken as proportional to the logarithm of the ratio of the intensities of these lines and the working curve is determined in a manner similar to that of Twyman and Hitchen.

The authors have, for a number of years, been using spectrographic methods for estimating small amounts of metals in various alloys, particularly nickel alloys, in connection with the development of nickel alloys containing barium by the AC Spark Plug Company. Since early in 1931 this method has been used continuously for the quantitative determination of barium in nickel alloys. During this time numerous checks by means of chemical analyses have shown that the spectroscopic determinations are fully as consistent and accurate as those made by chemical methods. This long-continued use

of a method of accurate quantitative analysis for a particular purpose clearly demonstrates the reliability and value of spectroscopic methods of quantitative analysis. The method has been used with equal success in determining silicon in steel, chromium in nickel, and magnesium, sodium, and potassium in various solutions, and seems capable of very general application.

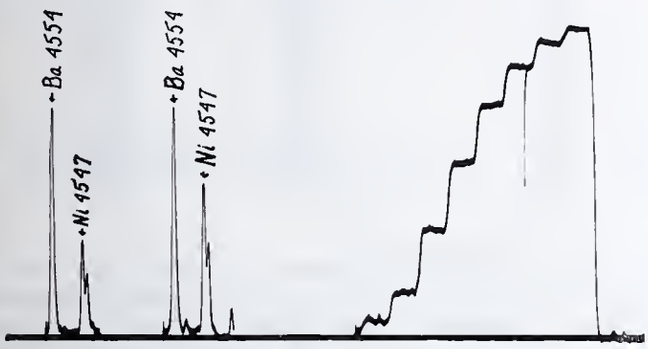

FIGURE 1. MICROPHOTOMETER RECORD OF A PORTION OF TWO SPECTROGRAMS AND OF A STEP-DIAPHRAGM CALIBRATION PATTERN, PHOTOGRAPHED ON THE SAME PLATE

One satisfactory method of determining the relative intensities of spectral lines from their relative densities or blackenings is that of Hansen (*1*, *7*, *9*, *15*). By means of a calibrated step diaphragm, a set of strips or bands is recorded on the photographic plate in which the relative intensity of the light is known. The measurement of the relative densities or blackenings of these bands gives a complete calibration curve for that particular plate, from which curve the relative intensities of any two spectral lines can be determined from a measurement of the relative densities or blackenings of the lines. Figure 1 is a reproduction of a microphotometer record of the relative blackenings of such a set of strips, together with those of a certain pair of barium and nickel lines taken from the same plate. It will be noted that the ratio of the blackenings of the barium and nickel lines changes markedly from one alloy to the other. The exposures were so timed that the blackening of the more intense line, in this case the barium line, did not exceed the maximum blackening of the straight-line portion of the characteristic curve of the plate. It is the experience of the authors that loss in accuracy of analysis occurs if the blackening of one of the lines exceeds this amount. The blackening of the weaker line may be less than the minimum blackening of the straight-line portion without a serious loss of accuracy.

From such a record as that of Figure 1 the curve of Figure 2 may be drawn. The slit width of the spectrograph should be sufficient so that the photographed lines are broad enough completely to intercept the beam of light in the microphotometer; otherwise the galvanometer deflections will not be proportional to the blackenings. Another convenient method of measuring the relative intensities of spectral lines is described by Thomson and Duffendack (*17*).

The choice of lines for a given analysis is determined by a number of considerations. When possible, lines should be chosen which lie in a region of slowly varying contrast of the plate used. When an element occurs in fairly considerable amounts in a mixture, one must guard against reversal of the lines and so lines which are not readily absorbed should be chosen. Some lines of an element are very strongly affected by the presence of even small amounts of another element, while other lines of the same element are not. These effects are most pronounced where close resonance exists between excited states of two elements, and so, when a mixture of several elements is being examined, the lines chosen should be tested for such effects. With a spark source, the relative intensities of arc and spark lines frequently show wide variations. These variations are not so great in an arc source, and it is sometimes possible to use the spark line of one element with the arc line of another, as was done in the case of the barium and nickel alloys used as an illustration in this report. Another troublesome matter is plate background. While corrections can be applied for background, none of them seems reliable and it is better to arrange the exposures so that the background is of negligible amount. The plates for Figure 3 and for all other measurements in this investigation had no appreciable background, the lines standing out on a clear plate.

STANDARDIZATION OF ARC

It is possible to make accurate analyses by the use of an arc source as well as a spark source. Upon investigation it was found that the relative intensities of a selected pair of spectral lines vary with the arc current in a manner indicated by the curve in Figure 3, drawn for the lines barium 4554.0 and nickel 4546.9. A similar relationship was found for the lines chromium 4289.73 and nickel 4401.55. It may be noted from Figure 3 that after the current reaches a certain value, the ratio of the intensities of a pair of lines changes quite slowly with the arc current. Thus, for currents greater than a certain amount, the ratio of intensities of selected lines becomes quite insensitive to such fluctuations of the current as exist in a normal arc. By working with such arcs, errors due to variations in the arc current become insignificant, and accurate analyses are possible.

The arc has the advantage over the spark in that the spectral lines, especially arc lines, are much more uniform over the length of the arc. Furthermore, the arc consumes more material of the electrodes than does a spark and hence gives a better average composition. A spark will seek out points on the cathode where materials of low work function may exist in small inclusions, whereas a strong arc strikes to a considerable fraction of the surface of the ends of the electrodes.

FIGURE 2. RELATION BETWEEN BLACKENING OF DEVELOPED PHOTOGRAPHIC PLATE AND EXPOSURE OF PLATE

METHOD OF ANALYSIS

The method of quantitative spectrographic analysis developed by the authors consists of the following steps:

I. FIXING OF EXCITATION CONDITIONS. An arc between electrodes consisting of or containing the material to be tested is used and the relation between the relative intensities of selected spectral lines and the arc current, as indicated in Figure 3, is determined. A value of arc current is chosen at which, for a small change in current, the change in relative intensity of the lines is small. A spark source may be used and standardized by the method of Gerlach and Schweitzer (*4*).

II. DETERMINING OF WORKING CURVE. A series of alloys, solutions, or mixtures is made in which the percentage composition of the material to be estimated is varied over the range chosen for the analysis. The value of the logarithm of the relative intensities of the selected lines is determined for each alloy in the series. In every case the spectrum is excited in the manner indicated by the experiments under I. These results are plotted as in Figure 4.

III. ANALYSIS OF AN UNKNOWN SPECIMEN. The spectrum of the unknown specimen is photographed in the manner determined under I and the logarithm of the relative intensities

of the selected lines is determined. The logarithm of the relative intensities of the spectral lines is applied to the working curve, Figure 4, and the percentage composition is read on the scale.

Discussion of Method

The method of analysis outlined above consists essentially in applying to this problem a correct method of photographic photometry. The calibration of each plate by putting upon it an intensity pattern is an essential feature of the method. No assumptions are made with respect to the reciprocity law or with respect to whether or not the line intensities fall on the straight-line part of the characteristic curve. It was only after the introduction of this step that accurate, repeatable, consistent analyses could be made.

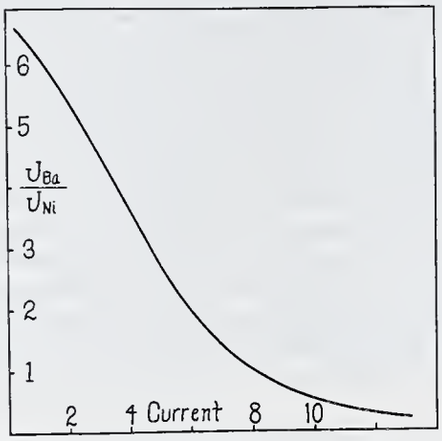

Figure 3. Relation between Arc Current and Relative Intensity of a Pair of Lines in Spectrum of a Barium-Nickel Alloy

One working curve suffices for a considerable range of percentage compositions of a given kind of material. Steps I and II need be performed but once for a particular kind of alloy, solution, or mixture. Step III alone must be repeated for each analysis. In this step, only one calibration curve (Figure 2) is necessary for a plate which may bear the spectrograms of a number, ten or twelve, of specimens to be analyzed. In the cases of barium-nickel and chromium-nickel alloys, spectrographic analyses have been found to be as accurate as chemical analyses and can be carried out in a small fraction of the time required for chemical analyses.

If a certain material is analyzed for several different elements, it is likely that the lines which will be used for the several elements will lie in more or less separated spectral regions. On account of the change in the contrast of the plate with wave length, separate calibration curves like that of Figure 1 will be needed. In such cases, it is desirable to put on the plate an intensity pattern which extends over all wave lengths. This can be done by means of the Hansen method coupled with the spectrograph and more conveniently by the method of Thomson and Duffendack. With such a pattern, calibration curves can be determined for any wave length desired.

Figure 4 shows two working curves for the estimation of barium, one for a nickel alloy and one for a nickel-copper alloy. In both these curves, the same pair of barium and nickel lines is used, and it is obvious that the addition of copper to the alloy affects the variation of the relative intensities of these lines with the percentage of barium. This illustrates a situation which is frequently encountered, as was noted by Twyman and Hitchen (*19*, *20*). Account must be taken of this effect and working curves are necessary for any given element in each type of alloy. If a second element also varies in amount in a given alloy, one must determine whether the extent of variation is sufficient to affect the working curve of the other test element.

Table I. Comparative Analyses of Barium-Nickel Alloys

Alloy Number	Barium: Chemical analysis	Barium: Spectroscopic analysis
	%	%
716	0.016	0.015
637	0.021	0.028
821	0.022	0.023
682	0.048	0.051
667	0.052	0.055
669	0.058	0.057
736	0.060	0.059
662	0.064	0.064
692	0.078	0.075
665	0.095	0.091
678	0.130	0.130
420	0.142	0.145
179	0.37	0.38
178	0.52	0.49

In order to indicate the degree of accuracy that may be attained in regular production practice, Table I gives some comparative analyses of the same specimens of barium-nickel alloys by spectroscopic and by chemical means. These analyses were chosen at random from a list of approximately three hundred. The mean deviations in the determination of the percentage of barium in a given specimen by spectroscopic methods were approximately the same as by chemical

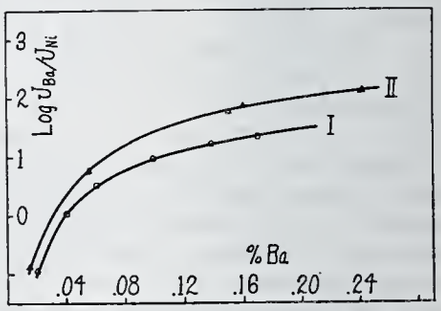

Figure 4. Relation between Percentage of Barium Alloys and Logarithm of Relative Intensity of a Pair of Lines in Spectra of the Alloys

I, barium-nickel alloy. II, barium-nickel alloy containing 20 per cent copper

methods and amount to ±0.001 per cent in the range from 0.01 to 0.150 per cent of barium. Some of the larger discrepancies between the spectroscopic and chemical determinations may be due to slight nonhomogeneities in the alloy.

Acknowledgment

The alloys used for the analyses mentioned in this paper were prepared by the AC Spark Plug Company and the chemical analyses were made in the company's laboratories. The authors wish to express their appreciation of the friendly coöperation of D. W. Randolph, director of research at the AC Spark Plug Company, and his assistants, and to thank the company for its financial support.

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Determination of Equivalent Acidity and Basicity of Fertilizers

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During the last few years there has been a general recognition of the acid-forming character of certain nitrogenous fertilizers. The amounts of limestone required to neutralize the acidity developed by these fertilizers are well established. The amount of acidity developed by mixed fertilizers, however, is not known; nor has it been possible to determine it satisfactorily.

It is readily evident from a consideration of the common nitrogen carriers used that mixed fertilizers are usually acid-forming. In an attempt to correct this condition some progressive fertilizer manufacturers have been using ground limestone instead of sand as the filler. This practice is sound economically and should be encouraged. Recent work by MacIntire et al. (*5*, *6*) shows that no loss of available phosphoric acid results from the use of the dolomitic limestone. Such a practice probably would not become general unless recognition were given to the value of the added limestone. Parker (*7*) has pointed out that if the use of limestone[1] is to be encouraged, a method must be developed that can be used to determine the limestone in mixed fertilizers and thus make possible the guarantee and chemical control of this desirable constituent of fertilizers.

With these considerations in mind this investigation was started with the purpose of developing a simple, quantitative laboratory method for determining the equivalent acidity or basicity of any fertilizer carrier or mixture. (Equivalent acidity may be defined as the acidity developed by the fertilizer, measured in terms of calcium carbonate required for its neutralization. Equivalent basicity refers to the basic residue left in the soil by fertilizers, expressed as equivalent calcium carbonate.)

Action of Fertilizers on Soil Acidity

Before discussing the method developed for determining the equivalent acidity or basicity of fertilizers, it seems desirable to review briefly the effect of fertilizers on soil acidity and the principles governing this action. A review of the investigations regarding the effect of fertilizers on soil reaction leads to the following conclusions:

1. The common potassium fertilizers such as kainit and muriate and sulfate of potash have no residual effect on soil reaction.
2. Phosphate fertilizers in which one of the three hydrogens of phosphoric acid is replaced by a base will in general have no permanent effect on soil acidity, whereas those in which more than one hydrogen is replaced by base will be basic in their effect on soil reaction. (For those phosphates in which the base is ammonia see next point.)
3. Fertilizers containing nitrogen in the form of ammonia or in a form subject to nitrification in the soil will produce acidity unless sufficient base is present to neutralize this acidity.
4. Nitrogenous fertilizers in which the nitrogen is in the nitrate form and combined with bases such as sodium or calcium will upon being utilized by plants result in decreased soil acidity.

The fact that potassium fertilizers do not have a residual effect on soil reaction is generally recognized. With regard to phosphate fertilizers, however, there has been some controversy. Most of the results obtained in long-time field experiments show that superphosphate slightly decreases or has no effect on soil acidity. In recent studies the writer has found that the action of phosphates on soil reaction will depend to some extent on the original acidity of the soil and that for cultivated soils of the humid region, the pH of which lie mostly between 5 and 6, superphosphate has no appreciable effect on soil reaction. Any method for determining the acidic or basic property of fertilizers should consequently consider monocalcium phosphate as neutral and the di- and tricalcium-phosphate as basic.

Nitrogenous fertilizers containing ammonia have been shown to be acid-forming because of the process of nitrification which takes place when the fertilizer is added to the soil (*8*). A method for determining the acidity resulting from ammonium fertilizers should consider the acidity that is developed when complete nitrification of the ammonia takes place. Although in some cases there is likely to be some absorption of the ammonia by the plant before being nitrified, this amount is probably small under average conditions.

The amount of acidity formed from ammonium sulfate was found (*8*) to be lower than that calculated on the assumption that all the nitrogen and sulfate would act as nitric and sulfuric acid, respectively. In these experiments conditions were very favorable for nitrification and the low values obtained were believed to be due to the action of the plant. Apparently plants absorb from calcium or sodium nitrate more of the nitrate ion than of the calcium or sodium ion. The result of such an action is to cause sodium and calcium nitrate to leave a basic residue in the soil and to reduce the acidity resulting from the nitrification of ammonia present in acid-forming fertilizers. From a calculation of the basic action of calcium and sodium nitrate on soils (*8*) it was found that 51 per cent of the base had been effective in reducing soil acidity, indicating that approximately one-half as much of the base had been absorbed by the plant as of the nitrate ion. It follows, therefore, that only one-half

[1] In this paper limestone includes both calcium limestone and dolomite. The latter is preferable in fertilizers, for it reacts less with superphosphate (MacIntire) and also serves as a source of magnesium.

of the potential nitric acid in ammonium sulfate is effective in increasing soil acidity. On this basis ammonium sulfate should develop only three-fourths of its potential acidity if plants are growing in the soil. This was approximately the value found in the Alabama experiments. The significance of this in connection with the development of a method will be shown later.

Acid-Base Balance of Fertilizers

The experimental results just summarized make possible a rather simple conception of the influence of fertilizers on soil acidity—namely, that differences in the effect of fertilizers on soil reaction are due to differences in their acid-base balance. Those fertilizers which have an excess of basic over acidic elements would reduce soil acidity, whereas those which have an excess of acidic over basic elements would increase soil acidity. In applying this conception, the following facts previously discussed must be considered:

1. Only one-third of the phosphoric acid should be considered acid-forming.
2. Since nitrogen in fertilizers is either in the nitrate form or in a form which is changed to nitrates through the process of nitrification, it should be considered an acidic element. Because of the action of plants, however, only one-half of the nitrogen should be considered acid-forming.

In determining the equivalent acidity or basicity of fertilizers, therefore, the following balance of elements is involved:

Acid-Forming Elements		Base-Forming Elements
Sulfur Chloride 1/3 of phosphorus 1/2 of nitrogen	versus	Calcium Magnesium Potassium Sodium

If the amounts of these various elements contained in the fertilizer are known, the residual effect of the fertilizer on soil acidity can readily be calculated. It would, of course, be possible to make individual determinations of these elements, but this would be time-consuming and not adapted to routine work. The method proposed makes possible a rapid determination of the excess of acid-forming or of base-forming elements in the fertilizer. From the values obtained the acidity or basicity equivalent of the fertilizer can readily be calculated.

Description of Method

The proposed method for determining the equivalent acidity or basicity of fertilizers consists essentially in titrating the excess of acidic or basic elements in the fertilizer after igniting to destroy the organic matter. The ignition process also serves to volatilize the nitrogen present in various combinations which, like the organic matter, would interfere with the titration. Sulfates, chlorides, and phosphates are retained by the addition of sodium carbonate. The detailed method adopted is as follows:

Weigh 1 gram of fertilizer, ground to pass through a 20-mesh sieve, into a small porcelain or Pyrex beaker, preferably of about 100 to 150 cc. capacity. Add exactly 10 cc. of an approximately 2 *N* solution of sodium carbonate containing 50 grams of sucrose per liter and thoroughly mix with the fertilizer. Evaporate to dryness on a steam or water bath. Then place beakers in a furnace heated to about 250° C. and gradually raise the temperature to 500° to 600° C. or to dull redness. Keep at this temperature for 1 hour, remove the beakers, allow them to cool, add 50 cc. of distilled water, cover with watch glass, and then add 30 cc. of *N* hydrochloric acid. The reaction may then be allowed to take place overnight, or the beakers can be heated to gentle boiling for about 10 minutes after the initial reaction has taken place in the cold, or they can be kept on steam or water bath for one-half hour. The residue is then removed by filtering, preferably by suction, or it can be allowed to settle out overnight, after transferring the contents of the beakers to 100-cc. sugar volumetric flasks and made up to volume. In the latter case 50 cc. of the supernatant liquid are removed for titration, while in the former the total extract is used. The excess acid in either case is titrated with *N* sodium hydroxide, using methyl red as an indicator and taking the first change in color as the end point of the titration. Erlenmeyer flasks of 250 cc. capacity are convenient for the titration when the solution has been diluted to about 150 cc. Ten drops of 0.2 per cent indicator solution are used.

Sugar is added to the fertilizer sample before ignition in order to help volatilize the nitrates which may be present in the fertilizer and which would not otherwise be driven off at the temperatures recommended. Although it was found that 0.25 gram of sugar volatilized all the nitrogen from a fertilizer containing 1 per cent of nitrate nitrogen, 0.5 gram is recommended in order to meet exceptional conditions. If it is desired to determine the equivalent basicity of such nitrate carriers as sodium or calcium nitrate, the use of carbon black is recommended, since a violent reaction takes place if sugar is used in large amounts in the presence of considerable nitrates. The use of equal quantities of carbon black and sodium nitrate was found satisfactory in completely volatilizing all the nitrates from this fertilizer material.

In order to calculate the amount of acid or base liberated by the fertilizer, it is necessary to run a blank on the sodium carbonate, since this solution is made up only approximately 2 *N*. The blank solution need not be evaporated or ignited, but it should be boiled gently to drive off the excess carbon dioxide after adding the acid and thus to sharpen the end point of titration. If more base is required in titrating the fertilizer solution than in titrating the blank, the fertilizer is acid-forming, while if less base is required by the fertilizer it is base-forming. Every cubic centimeter of base required by the fertilizer in excess of that required by the blank shows an acidity equivalent to 100 pounds of calcium carbonate per ton, while every cubic centimeter of base required in lower amounts by the fertilizer than by the blank shows a basicity equivalent to 100 pounds of calcium carbonate per ton.

In addition to the acidity or basicity of the fertilizer thus given, the acidity due to the nitrogen in the fertilizer must be considered. On the basis that one-half the nitrogen in the fertilizer is acid-forming when applied to soils in which crops are growing, the amount of acidity due to the nitrogen is obtained by multiplying the percentage of nitrogen in the fertilizer by 35.7. This gives the acidity equivalent to pounds of calcium carbonate per ton of fertilizer. The algebraic sum of the acidity due to the nitrogen and the acidity or basicity from the non-nitrogenous portion of the fertilizer obtained by titration gives the net equivalent acidity or basicity of the fertilizer.

End Point of Titration

As previously explained, only one-third of the phosphoric acid should be considered acid-forming. It has been shown by Britton (*1*) that in the titration of phosphoric acid the first hydrogen of the acid is neutralized at a pH of about 5.5. Since the transition range of methyl red is between pH 5.0 and 6.0, this indicator was selected for determining the end point of titration. That it gives the desired end point is shown by the data in Table I. It will be noted that the equivalent basicity values of mono-, di-, and tricalcium phosphate agree well with the theoretical values. Monocalcium phosphate reacts neutral according to this method.

The end point taken was the first change in color from reddish pink to a slightly orange-pink. In order to observe this first change in color more easily, especially with fertilizers containing a large amount of phosphorus, it was found desirable to use a standard for comparison. The

standard should contain excess acid equivalent to a few drops of 0.1 *N* hydrochloric acid.

Table I. Equivalent Basicity Obtained for Mono-, Di-, and Tricalcium Phosphates as Compared with Theoretical Values

Phosphate Compound	P_2O_5	Equivalent Basicity[a] Found	Theoretical[b]
	%		
Monocalcium phosphate	56.2	−2	0
Dicalcium phosphate	52.2	739	735
Tricalcium phosphate	45.6	1258	1284

[a] Lb. $CaCO_3$ per ton.
[b] The theoretical values were obtained by considering one-third of the phosphoric acid as acid-forming. The sample of dicalcium phosphate used contained no water of crystallization.

Losses during Ignition

It has been shown by various investigators that in ashing plant material for determining their acid-base balance there may be a loss of chlorides and sulfates during the ignition. Frear (*3*) suggested the use of magnesium nitrate to prevent such losses. It was found in the present study, however, that the use of magnesium nitrate does not prevent the loss of chlorides from fertilizers during ignition. Sodium carbonate, however, was found to prevent the loss of chlorides, sulfates, and phosphates even when the temperature was raised to 650° C., the highest temperature studied. That no loss of anions takes place is evidenced by the data given in Tables I, V, and VIII which show that the equivalent acidity values found for calcium and ammonium phosphate, ammonium sulfate, and complete fertilizers agree very well with the theoretical.

Effect of Different Ignition Temperatures

Since no special oxidizing agent is used to aid the oxidation of the organic matter, it would be expected that with some organic fertilizers heating to the temperatures recommended would not destroy all the carbon. Such was found to be the case. The effect of heating to higher temperatures was therefore studied. In Table II are given the data obtained by heating various organic fertilizer materials to different temperatures. In all cases a considerable amount of carbon was left when ignition was carried out at the lower temperatures—that is, approximately 500° to 600° C. When ignited at temperatures ranging from 650° to 750° C., however, relatively little or no carbon remained. It will be noted that the equivalent basicity of the fertilizers at the two temperatures agreed very closely. Inasmuch as there is more etching of the beakers when ignition is carried out at high temperatures, the lower temperatures are recommended. Silica or platinum crucibles were used when the ignition was above 650° C.

The etching of the beakers caused by sodium carbonate during ignition at temperatures of 650° C. or below could not be found to have any influence on the titration value.

Equivalent Acidity and Basicity

Phosphorus and Potassium Fertilizers. The equivalent acidity or basicity of phosphate fertilizers determined according to the proposed method is given in Table III. Two of the superphosphate samples were slightly acidic, while two were slightly basic. The high value obtained for sample 102 probably is due to the presence of limestone or of some undecomposed rock phosphate. This would seem to be indicated by the fact that the sample shows a higher content of unavailable phosphate than do the others.

Table II. Effect of Different Ignition Temperatures on Equivalent Basicity of Organic Fertilizers

Fertilizer No.	Fertilizer Material	Low Temperatures	Equivalent basicity[a]	High Temperatures	Equivalent basicity[a]
		° C.		° C.	
1	Animal tankage	510	294	650	300
7	Fish scraps	540	161	730	153
21	Goat manure	540	490	650	482
18	Dried blood	590	16	730	0
4	Packing-house tankage	590	411	700	410
23	Castor pomace	540	81	700	60
9	Acid fish	540	153	730	150

[a] ≈ lb. $CaCO_3$ per ton.

Table III. Equivalent Acidity or Basicity of Different Phosphate Fertilizers

Fertilizer No.	Phosphate Fertilizer	P_2O_5 Available	Total	Equivalent[a] Acidity	Equivalent[a] Basicity
		%	%		
101	Superphosphate	20.10	20.65	..	15
102	Superphosphate	20.48	21.75	..	62
103	Superphosphate	17.30	17.45	17	..
104	Superphosphate	20.23	20.46	14	..
105	Steamed bone meal	9.18	34.56	..	1214
106	Bone ash	3.45	40.15	..	1413
107	Limed superphosphate	6.53	17.30	..	424
108	Texas bone	12.60	23.16	..	852
109	Precipitated bone	41.85	42.03	..	586
110	Tenn. brown rock phosphate	1.98	33.86	..	1122

[a] ≈ lb. $CaCO_3$ per ton.

The other phosphate fertilizers are all basic. Bone ash is the most basic, a ton of the material being equivalent to 1413 pounds of pure calcium carbonate or ground limestone. The limed superphosphate gives a value within 15 pounds of the calculated value based on the proportions of hydrated lime and superphosphate used in making the mixture. The method shows rock phosphate to be basic in accordance with the fact that the phosphate is there in the tricalcium form. In soils, however, the neutralizing action of rock phosphate has been found to be very slow as compared with the neutralizing action of di- and tricalcium phosphate (*9*). For this reason this method may give it a slightly high basicity value.

In Table IV are given the equivalent acidity values obtained from several samples of superphosphate before and after ammoniation. Ammoniation has not affected the titration value or the acidity resulting from the non-nitrogenous portion of the fertilizer. Although ammonium sulfate is formed during ammoniation, there is an accompanying formation of di- and tricalcium phosphates which are basic. Ammoniation increases the net equivalent acidity of superphosphate because the added ammonia produces acid on being nitrified in the soil.

Potassium chloride and sulfate were found to be practically neutral as indicated by the proposed method.

Various Nitrogenous Fertilizers. Because nitrogenous fertilizers are primary factors in determining the influence of mixed fertilizers on soil reaction, it seemed

Table IV. Equivalent Acidity of Superphosphates and Ammoniated Superphosphates

Fertilizer No.[a]	Fertilizer	P_2O_5 Available	Total	Nitrogen	Titration Values Equivalent acidity[b]	Equivalent basicity[b]	Equivalent Acidity[b] Due to Nitrogen	Net Equivalent Acidity[b]
		%	%	%				
111	Superphosphate	20.23	20.46	0.0	14	..	0	14
112	Ammoniated superphosphate	18.61	19.86	2.69	19	..	96	115
113	Ammoniated superphosphate	11.61	18.83	6.53	9	..	233	242
114	Superphosphate	19.77	20.09	0.0	24	..	0	24
115	Ammoniated superphosphate	16.09	19.00	4.71	32	..	168	200

[a] 112 and 113 were made by ammoniating 111, and 115 by ammoniating 114.
[b] ≈ lb. $CaCO_3$ per ton.

TABLE V. EQUIVALENT ACIDITY OR BASICITY OF VARIOUS INORGANIC NITROGEN FERTILIZERS

Fertilizer Material	Nitrogen	Titration Values: Equivalent acidity[a]	Titration Values: Equivalent basicity[a]	Equivalent Acidity[a] Due to Nitrogen	Net Equivalent Acidity [≈ lb. $CaCO_3$]: Per ton of fertilizer	Net Equivalent Acidity [≈ lb. $CaCO_3$]: Per unit of nitrogen	Net Equivalent Basicity [≈ lb. $CaCO_3$]: Per ton of fertilizer	Net Equivalent Basicity [≈ lb. $CaCO_3$]: Per unit of nitrogen
	%							
Ammonium sulfate	21.1	1496	..	753	2249	107	..	..
Ammonium chloride	26.1	1854	..	932	2786	107	..	..
Monoammonium phosphate	12.1	860	..	432	1292	107	..	..
Ammo-Phos	11.0	704	..	393	1097	100	..	..
Urea	46.6	16	..	1664	1680	36	..	..
Sodium nitrate	16.4	..	1168	585	..	...	583	36
Cal-Nitro	16.0	..	917	571	..	...	346	22
Calcium cyanamide	22.0	..	2030	785	..	...	1245	57

[a] ≈ lb. $CaCO_3$ per ton.

TABLE VI. EQUIVALENT ACIDITY OR BASICITY OF VARIOUS ORGANIC FERTILIZERS

Fertilizer No.	Fertilizer Material	Nitrogen	Titration Value Equivalent Basicity[a]	Equivalent Acidity Due[a] to Nitrogen	Net Equivalent Acidity [≈ lb. $CaCO_3$]: Per ton	Net Equivalent Acidity [≈ lb. $CaCO_3$]: Per unit of nitrogen	Net Equivalent Basicity [≈ lb. $CaCO_3$]: Per ton	Net Equivalent Basicity [≈ lb. $CaCO_3$]: Per unit of nitrogen
		%						
1	Animal tankage	9.12	297	326	29	3	...	...
2	High-grade tankage	8.39	178	300	122	15	...	...
3	Low-grade tankage	4.28	770	153	...	..	617	144
4	Packing-house tankage	6.00	413	214	...	..	199	33
5	Garbage tankage	2.50	223	89	...	..	134	54
6	Process tankage	7.38	36	263	227	31	...	...
7	Fish scrap	9.25	161	330	169	18	...	...
8	Fish scrap	8.93	297	319	22	2	...	...
9	Acid fish	6.00	153	226	73	12	...	...
10	Cottonseed meal	6.76	47	241	194	29	...	...
11	Cottonseed meal	6.71	50	240	190	28	...	...
12	Tobacco stems	2.77	337	99	...	..	238	86
13	Tobacco stems	1.40	548	50	...	..	498	356
14	Peruvian guano	13.80	224	493	269	19	...	...
15	Peruvian guano	13.90	222	496	274	20	...	...
16	Whale guano	9.70	249	336	87	9	...	...
17	Dried blood	13.00	37	488	451	35	...	...
18	Dried blood	13.41	16	479	463	35	...	...
19	Cocoa shell meal	2.75	131	98	...	..	33	12
20	Humus	2.80	397	100	...	..	297	106
21	Goat manure	1.31	490	47	...	..	443	338
22	Castor pomace	4.77	82	170	88	18	...	...
23	Castor pomace	4.77	81	170	89	18	...	...
24	Milorganite	7.00	12	250	238	34	...	...

[a] ≈ lb. $CaCO_3$ per ton.

desirable to determine the equivalent acidity or basicity of some of the common nitrogen carriers, especially of those whose action on soil acidity is known. The results obtained are given in Table V. The equivalent acidity or basicity is expressed in terms of pounds of calcium carbonate per ton of fertilizer and also pounds of calcium carbonate per unit of nitrogen. On the latter basis sulfate of ammonia, ammonium chloride, and monoammonium phosphate are equally acid-forming and require 107 pounds of calcium carbonate per unit of nitrogen. This is in agreement with theoretical values and with the results obtained in soil studies (*8*). As is to be expected, the titration value for urea is practically zero, the acidity given for urea being due to the nitrogen. Sodium nitrate gave an equivalent basicity by titration of 1168 pounds as compared with the theoretical value of 1170 pounds. When the nitrogen is considered, the equivalent basicity per ton is 583 and per unit of nitrogen, 36. Cal-Nitro was found to have an equivalent basicity of 22 pounds of calcium carbonate per unit of nitrogen. This value is slightly lower than the theoretical value based on the statement that the material is an equal mixture of ammonium nitrate and calcium carbonate. Calcium cyanamide is the most basic nitrogenous fertilizer studied. The value obtained is in close agreement with the claims by the manufacturer as to its total calcium content.

These results show that the method proposed gives values for nitrogen carriers that are in close agreement with the theoretical values and with the result of soil studies.

ORGANIC FERTILIZERS. The equivalent acidity or basicity of various organic fertilizers are given in Table VI. If the titration values or the mineral acid-base balance values alone were considered, all the fertilizers would be base-forming. When the nitrogen is taken into account, however, most of the organic fertilizers show a net equivalent acidity. The significant fact is that there is a wide variation in their acid-forming properties and that some fertilizers are basic.

Different samples of animal tankage vary markedly in their acid-base balance. Samples 1 and 2 show a small equivalent acidity value, whereas 3 and 4 are basic. This difference in different samples of animal tankage is probably due to variations in the amount of ground bone contained. That samples 3 and 4 contain more bone is indicated by the fact that their total phosphoric acid content is 19.6 and 12.8 per cent, respectively, whereas samples 1 and 2 contain 9.0 and 6.2 per cent of phosphoric acid, respectively. Differences in the net equivalent acidity of different samples of fish scrap are probably also due to variations in the percentage of bones in the material.

Two samples of cottonseed meal were found to be very similar in their net equivalent acidity. This was also true for different samples of Peruvian guano, dried blood, and castor pomace. Apparently these products are rather constant in composition. Cottonseed meal was found to have an equivalent acidity per unit of nitrogen about three-fourths as high as urea, whereas that for dried blood was about the same as for urea. It is significant that the acidic property of dried blood as shown by this method is in agreement with long-time field experiments (*2*, *4*). Peruvian guano and castor pomace are shown to have a net equivalent acidity per unit of nitrogen about one-half as high as urea, whereas Milorganite shows a value about the same as urea. The two samples of tobacco stems studied both show a high equivalent basicity, sample 13 being particularly basic.

It is evident from these results that no one value can be taken for the effect of different organic fertilizers on soil acidity. It is possible, however, that if a large number of samples were studied, definite values could be established for some of the important organic nitrogen carriers.

MIXED FERTILIZERS. Fourteen different fertilizer samples were prepared as described in Table VII. Seven of the samples were made up with sand as the filler, while the other seven were exactly the same except that dolomitic limestone

Table VII. Composition of Fertilizer Mixtures

Fertilizer No.	Fertilizer Analysis	Nitrogen Source	Nitrogen Per cent of total nitrogen	Phosphoric Acid Source	Phosphoric Acid Per cent of total P_2O_5	Potash Source	Potash Per cent of total K_2O	Filler[a] Lb./ton
1A and 1B	4–12–4	Ammonium sulfate	100	Superphosphate	100	Muriate of potash	100	314
2A and 2B	4–12–4	Ammonium sulfate Calcium cyanamide	75 25	Superphosphate	100	Muriate of potash	100	317
3A and 3B	4–12–4	Ammonium sulfate Nitrate of soda	75 25	Superphosphate	100	Muriate of potash	100	287
4A and 4B	4–12–4	Ammonium sulfate Animal tankage	75 25	Superphosphate Animal tankage	91.7 8.3	Muriate of potash	100	287
5A and 5B	6–18–6	Ammonium sulfate Ammonium phosphate	59 41	Ammonium phosphate	100	Muriate of potash	100	992
6A and 6B	6–15–9	Ammonium sulfate Ammonium phosphate Cottonseed meal Nitrate of soda	31 49 10 10	Ammonium phosphate	100	Muriate of potash	100	816
7A and 7B	4– 8–7	Ammonium sulfate Ammonium phosphate Tobacco stems	36 39 25	Ammonium phosphate	100	Muriate of potash Tobacco stems	60 40	289

[a] Sand was used as the filler in the A samples, and dolomite in the B samples.

Table VIII. Equivalent Acidity or Basicity of Various Mixed Fertilizers and Recovery of Added Limestone Used as Filler

Fertilizer No.	Titration Values: Equivalent basicity[b] Theoretical	Equivalent basicity[b] Found	Equivalent acidity[b] Theoretical	Equivalent acidity[b] Found	Recovery of Added Limestone by Analysis: Limestone added to fertilizer (Lb./ton)	Limestone recovered by analysis (Lb./ton)	Net Equivalent Acidity[a] or Basicity: Equivalent acidity[b]	Equivalent basicity[b]
1A	...	...	285	284	..	..	427	...
1B	44	50	...	...	329	334	93	...
2A	...	...	121	118	..	..	361	...
2B	212	222	...	...	333	340	...	79
3A	...	...	143	132	..	..	275	...
3B	158	162	...	...	301	294	...	19
4A	...	...	182	172	..	..	315	...
4B	119	136	...	...	301	308	7	...
5A	...	...	429	418	..	..	632	...
5B	612	633	...	...	1041	1051	...	419
6A	...	...	291	277	..	..	491	...
6B	565	572	...	...	856	849	...	81
7A	101	104	...	...	..	..	39	...
7B	406	412	...	...	305	308	...	269

[a] The acidity due to the nitrogen was calculated to be 143 lb. $CaCO_3$ per ton for samples 1A to 4B, inclusive, 214 lb. $CaCO_3$ for 5A to 6B, inclusive, and 143 lb. $CaCO_3$ for 7A and 7B.
[b] = lb. $CaCO_3$ per ton.

was used instead of sand. In Table VIII are given the theoretical titration values of the fertilizer, compared with the values obtained by the method described. The agreement is found to be very satisfactory, the difference in most cases being less than 15 pounds of calcium carbonate per ton of fertilizer.

Since the only difference between the respective A and B samples is that sand was used in the former and dolomite in the latter, it is possible to calculate how closely the method indicates the amount of dolomite that has been added. In the sixth column of Table VIII are given the amounts of dolomite, expressed as calcium carbonate added to each fertilizer, and in the seventh column, the greater basicity of the B over the A samples obtained by analysis. A comparison of the values shows good agreement. It is thus evident that the basicity resulting from the use of limestone as filler is accurately shown by the method.

In Table VIII is also given the net acidity or basicity of these mixed fertilizers after considering the acidity due to the nitrogen. It will be noted that all the A samples, where sand was used as the filler, are acid-forming. The net equivalent acidity varies from 39 pounds of calcium carbonate per ton for sample 7A to 632 pounds for sample 5A. On the other hand, the use of dolomite instead of sand as filler has changed these fertilizers from acid-forming to base-forming in all cases except 1B and 4B, and in these the equivalent acidity has been greatly reduced. The use of limestone instead of sand in commercial mixtures should form in many cases a more basic product than was obtained with these samples, since the latter are higher in total plant food than are many commercial mixtures.

General Discussion

The proposed method makes possible a recognition of the influence of mixed fertilizers on soil reaction. At the present time there is no such recognition either by state control officials or by most fertilizer manufacturers. Since the acidic or basic action of any mixed fertilizer is one of its important properties, it should be recognized as such by state control laws governing the sale of fertilizer. Fertilizer manufacturers could be permitted or required to state on the fertilizer tag or bag the equivalent acidity or basicity of the fertilizer just as is the percentage of nitrogen, phosphoric acid, and potash. The guaranteed equivalent acidity or basicity of the fertilizer would then be subject to verification for correctness by the state control laboratories. This would not involve much added expense, inasmuch as the method proposed is simple, is well adapted to routine analysis, and does not require equipment that is not already found in most control laboratories.

The recognition of the acidic or basic properties of fertilizers by state fertilizer laws would encourage the production of nonacid-forming fertilizers. At the present time most of the nitrogen carriers used in mixed fertilizers are acid-forming. For example, a calculation made of the nitrogen carriers used in the mixed fertilizers produced by three of the leading companies which operate in West Virginia show that an average of 71 per cent of the nitrogen was derived from the two most acid-producing sources—namely, ammonium sulfate and monoammonium phosphate. The remainder was derived from miscellaneous acid-forming carriers and some basic nitrogen carriers. By the use of limestone instead of

sand, now used as filler, the acidity produced by these mixed fertilizers could easily be neutralized. Those manufacturers who use limestone or produce base-forming fertilizers would then get credit for the added value of their products and the farmer would be protected in that he would know the acid- or base-forming properties of the fertilizers. Moreover, economy would result from the saving of freight on the sand or inert material now used as filler in mixed fertilizers.

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Colorimetric Determination of Fluoride in Water Using Ferric Chloride

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A COLORIMETRIC method for the determination of fluoride in water, recently described (*1*), is based on the fact that the intensity of the color produced with thiocyanate by a given amount of iron in the presence of fluoride is less than that produced in the absence of fluoride, by an amount depending on the quantity of fluoride present if there is an excess of iron. By determining colorimetrically the excess of iron reacting with ammonium thiocyanate, the quantity withdrawn by the fluoride from a given amount of iron may be found by difference and its equivalent in fluoride read from a curve which has been made by plotting definite amounts of fluoride against the iron they withdraw from the amount of iron used in the determination.

In a volume of about 75 cc. 0.375 mg. of iron (5 cc. of a standard ferric chloride solution containing 0.075 mg. of iron per cc.) produces about as deep a color as can be read in a Schreiner colorimeter and was taken as the amount of iron to be used. On this amount of iron 0.25 mg. of fluoride produces a marked fading and even as little as 0.025 mg. produces a fading that can be detected in a colorimeter. This degree of sensitivity permits the use of small volumes of water, 50 or 100 or even 25 cc., if the fluoride content of the sample is more than 4 parts per million.

Table I. Fluoride Found by Subtracting Iron Withdrawn by Sulfate from Total Iron Withdrawn

SO_4 as Na_2SO_4	Total Fe Withdrawn	Fe Withdrawn by SO_4	Fe Left for F	Fluoride Added	Fluoride Found
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
5.0	0.049	0.020	0.029	0.025	0.03
10	0.049	0.030	0.019	0.025	0.02
25	0.082	0.065	0.017	0.025	0.02
50	0.115	0.105	0.010	0.025	0.01
100	0.170	0.160	0.010	0.025	0.01
50	0.175	0.105	0.070	0.10	0.08
75	0.191	0.140	0.051	0.10	0.06
100	0.212	0.160	0.052	0.10	0.06
10	0.159	0.03	0.129	0.20	0.17
25	0.195	0.065	0.130	0.20	0.17
50	0.217	0.105	0.112	0.20	0.14
75	0.212	0.140	0.072	0.20	0.075

In Figure 1 fluoride is plotted against iron withdrawn. The amount of iron withdrawn does not increase directly with increase in fluoride. Smaller quantities of fluoride cause, proportionately, a much greater bleaching than larger quantities. Under the present condition, however, the iron withdrawn from reactivity with thiocyanate—that is, the bleaching effect of a given amount of fluoride—is definite and reproducible although not a straight-line function. In the presence of 0.45 mg. of fluoride the color is more yellow than red and it is inadvisable to extend the curve beyond this point.

Table II. Determination of Fluoride in Artificial Waters

SO_4 as $CaSO_4$	SO_4 as $MgSO_4$	SO_4 as Na_2SO_4	Total SO_4	Cl as $CaCl_2$	Cl as $MgCl_2$	Cl as NaCl	Total Cl	Fluoride Added	Fluoride Found
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
7.0	..	..	7.0	26.5	16.5	2.0	45.0	0.35	0.32
								0.20	0.20
								0.025	0.025
								0.00	0.00
..	1.5	8.5	10.0	2.5	..	17.7	20.2	0.35	0.32
								0.20	0.20
								0.025	0.02
								0.00	0.00
..	3.0	1.0	4.0	16.0	..	4.0	20.0	0.35	0.35
								0.25	0.24
								0.025	0.025
								0.00	0.00
..	3.1	16.8	19.9	9.2	..	16.5	25.7	0.35	0.325
								0.20	0.20
								0.025	0.025
								0.00	0.00
..	..	20.0	20.0	1.4	1.2	29.6	32.2	0.35	0.33
								0.20	0.20
								0.025	0.020
								0.00	0.00
4.0	1.5	..	5.5	6.3	2.0	27.5	35.0	0.35	0.34
								0.20	0.20
								0.025	0.025
								0.00	0.00
16.4	13.5	2.6	32.5	13.0	..	7.6	20.6	0.35	0.31
								0.20	0.18
								0.025	0.02
								0.00	0.00
..	..	2.5	2.5	10.6	3.2	7.6	21.4	0.35	0.36
								0.20	0.21
								0.025	0.03
								0.00	0.00
4.7	4.4	10.9	20.0	3.2	..	2.2	5.4	0.35	0.34
								0.20	0.20
								0.025	0.03
								0.00	0.00
..	1.0	..	1.0	2.6	..	0.4	3.0	0.35	0.36
								0.20	0.21
								0.025	0.020
								0.00	0.00

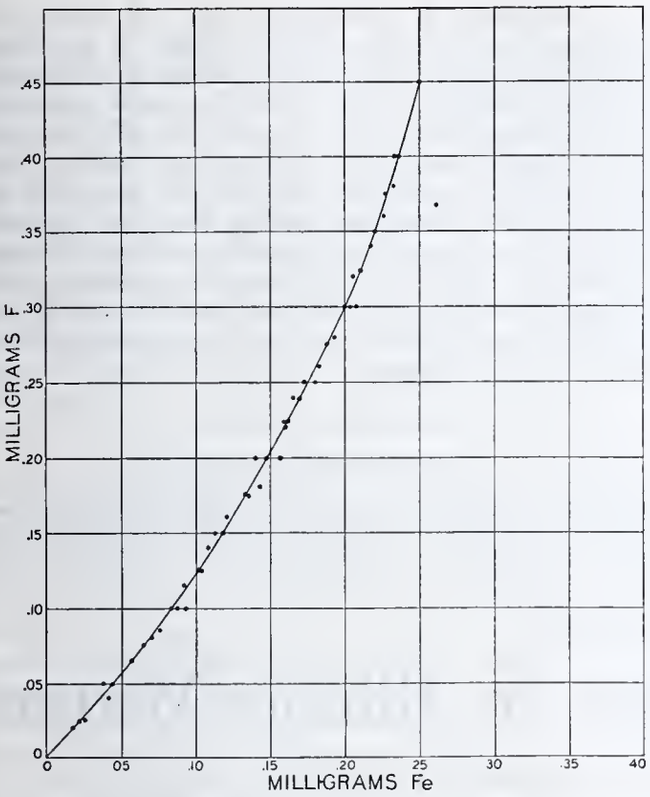

FIGURE 1. IRON WITHDRAWN FROM REACTIVITY WITH THIOCYANATE BY DIFFERENT QUANTITIES OF FLUORIDE

The iron withdrawn from reaction with thiocyanate by the other acidic constituents of natural waters was determined in the same manner as for fluoride. Most natural waters do not contain enough phosphate or borate in the volume used for the determination to interfere with its accuracy. Nitrate present in quantities as great as 75 mg. in the volume used has no effect on the color; 100 mg. effect a fading which can just be detected in the colorimeter and which is equivalent to only 0.01 mg. of fluoride. For this reason nitric acid was chosen to neutralize the alkalinity of the water sample. The quantities of sulfate and chloride likely to be found in water, however, have a decided bleaching effect on the intensity of color produced by 0.375 mg. of iron with thiocyanate. The effect of sulfate and chloride is the same whether they are present as calcium, magnesium, or sodium salts. In the earlier paper this effect of sulfate and chloride was corrected by subtracting, by reference to the curves, the iron withdrawn by the amounts of sulfate and chloride in the unknown from the total iron withdrawn. On further study, however, this was found to give erroneous results particularly for the larger concentrations of sulfate (as shown in Table I) because, in the presence of sulfate and chloride, the effect of the fluoride is not on 0.375 mg. of iron, on which the curve is based, but on 0.375 mg. minus the amount taken by sulfate and chloride. All three are competing for the iron. If, however, the amounts of iron withdrawn by the amounts of sulfate and chloride in the sample are added to the sample in addition to the 0.375 mg. of iron regularly added, the effect of the sulfate and chloride is counteracted and the effect of the fluoride is on 0.375 mg. of iron. This was proved by a number of tests in which the effect of different amounts of sulfate and chloride in samples containing no fluoride was counteracted in this way (shown in Table II). The resultant red color was equivalent, in all tests, to 0.375 mg. of iron. If, however, the sample contains much more than 50 mg. of sulfate or 100 mg. of chloride, this does not hold true. So much excess iron must be added that the bleaching effect is on 0.5 or 0.6 mg. of iron and not on 0.375.

The possibility that iron in solution in the sample might increase the color with ammonium thiocyanate and counteract the effect of fluoride is negligible. Examination of more than 650 analyses of waters from all parts of the United States indicates that practically all alkaline waters when analyzed contain in solution less than 0.10 part per million of iron—that is, less than 0.005 mg. of iron in 50 cc.

The details of the procedure follow:

Neutralize the alkalinity of 50 cc. of the sample of water contained in a comparison tube with 0.05 *N* nitric acid. Do not add an indicator but calculate from the alkalinity determination the amount of acid necessary to neutralize the volume of water used. If the alkalinity is high, use a stronger solution of nitric acid (0.02 *N*) in order to keep the volume of the neutralized sample within 60 cc. Add 5 cc. of ferric chloride solution (1 cc. = 0.075 mg. of iron, with 30 cc. of *N* hydrochloric acid to a liter) plus the amount necessary (by reference to the curves) to counteract the effect of the sulfate and chloride present and 10 cc. of ammonium thiocyanate (24 grams in a liter). Make the volume up to about 75 cc. and mix well.

Compare in a Schreiner colorimeter with a standard containing a known amount of iron (2 to 5 cc. of ferric chloride solution, the amount depending on the depth of color of the sample) and 10 cc. of ammonium thiocyanate solution in the same volume. Subtract the amount of iron found from 0.375 to get the amount withdrawn. Its equivalent in fluoride may be read from the curve (Figure 1). The ammonium thiocyanate should be added to the sample and standard at the same time and the comparison made immediately. The color of the standard should not be over 50 per cent greater or less than the color of the sample. If the color of the sample is too weak to be compared with a 2-cc. standard—that is, if the sample contains more than 0.40 mg. of fluoride—a smaller sample should be taken.

The sample used for the determination should not contain more than 50 mg. of sulfate or 100 mg. of chloride. If it contains less than 2.5 mg. of sulfate and/or 5.0 mg. of chloride, iron in excess of 0.375 need not be added.

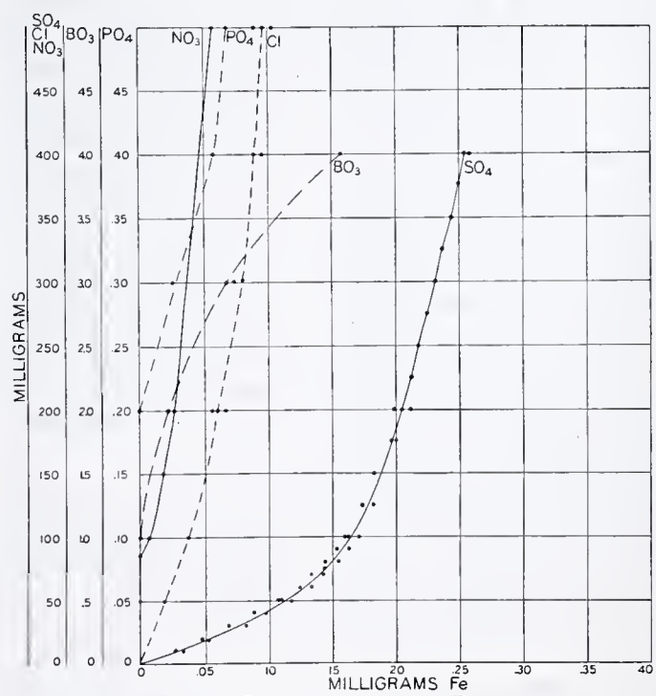

FIGURE 2. IRON WITHDRAWN FROM REACTIVITY WITH THIOCYANATE BY DIFFERENT QUANTITIES OF OTHER ACIDIC RADICALS FOUND IN WATER

It is advisable that each analyst work out his own curves for fluoride, sulfate, and chloride.

The accuracy of the method was checked by adding 0.025, 0.20, and 0.35 mg. of fluoride to artificial waters containing the sulfate and chloride salts of sodium, calcium, and magnesium in different combinations and amounts. The results are shown in Table II.

One hundred and thirty samples of ground and surface water from 28 states, tested by this method, ranged in fluoride content as follows: 0 to 0.5 part per million, 50; 0.5 to 1.0 part, 38; 1.0 to 2.0 parts, 25; 2.0 to 3.0, 11; and

more than 3.0, 6. The highest fluoride found, 5.6 parts, was in a sample from a hot spring in California.

If preferred, standards made by adding known quantities of fluoride, 0.10 to 0.40 mg., to 5 cc. of ferric chloride solution and 10 cc. of ammonium thiocyanate in the same volume might be used, preparing the samples as already described. This affords a direct determination of fluoride against fluoride standards.

By using such fluoride standards, and by adding to the standards the quantities of sulfate and chloride (as sodium salts) contained in the volume of sample used, this method may be applied to the determination of fluoride in sea waters, brines, or any water containing more than 2500 parts per million of sulfate or more than 5000 parts of chloride. For such waters, however, 10 cc. of ferric chloride must be added to both sample and standard instead of the 5 cc. used when the effects of sulfate and chloride are counteracted by the addition of ferric chloride. This is necessary in order to have enough iron left for the fluoride after the sulfate and chloride have been satisfied.

This modification is recommended only for highly concentrated waters. It is not advisable to use it in preference to that in which the effects of these constituents are counteracted by the addition of ferric chloride for waters containing less than 2500 parts per million of sulfate or 5000 parts per million of chloride because (1) if 5 cc. of ferric chloride solution are used in sample and standard, the iron left for fluoride after the sulfate and chloride have been satisfied may be so reduced as greatly to restrict the fluoride range and sensitivity; (2) if 10 cc. are used the color in water containing low sulfate, chloride, and fluoride would be too deep to read; and (3) a different set of standards might be required for each sample.

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Determination of Fluorides in Illinois Waters

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An adaptation of the volumetric thorium precipitation method has been found to be the most reliable for the quantitative examination of waters for fluorides. The fluoride content of a number of Illinois waters has been determined by the use of this method.

From the data obtained so far it seems that the waters containing the greater quantities of fluorides are those which are found in and around the northeastern and northwestern part of the Illinois coal basin. All of these waters run high in nonincrusting solids. To date the results have not shown fluorides to be characteristic of any one stratum since they are found in waters associated with rocks of Pennsylvanian, Silurian, and Ordovician age.

Mottled tooth enamel is caused by the continued ingestion of fluorides during the period the teeth are being formed (*8*, *18*, *19*). Mottled teeth have been found in practically every country. This condition is endemic over large areas in the southwestern part of the United States and is frequently found in other sections (*8*, *11*, *12*, *14*). Studies already published have largely limited the primary sources of fluorides in the diet to that found in drinking waters (*11–13*, *18*, *19*). Bauxite, Ark., and Oakley, Idaho, have discarded abundant water supplies in favor of others containing less fluorides (*12*), and other cities are considering similar action. The exact minimum concentration of fluorides that will cause mottled teeth is not known. It has been reported by some to be about 2.0 p. p. m. (*21*) while others claim it to be about 1.0 p. p. m. (*15*).

Lack of agreement in results obtained in this and other laboratories while analyzing waters for small quantities of fluorides, using methods reported in the literature, together with the fact that extremely little is known concerning the fluoride content of Illinois waters, led the Water Survey to initiate the following investigation. This is strictly a chemical study; no attempt has been made by the authors to correlate the presence or absence of mottled teeth with the fluoride content of the Illinois waters which have been examined.

Of the numerous methods found in the literature for the quantitative determination of fluorides, there seem to be only a few which might be utilized to determine the small quantities (0 to 15 mg. per l.) found in waters. Gravimetric and colorimetric methods are fraught with many difficulties and uncertainties (*5*, *9*, *11*, *16*, *22*, *24*, *26*, *27*). Likewise, the concentration, drying, and distillation of silicon fluoride from dry residues in the presence of sulfuric acid and silica (*17*) with subsequent determination of the soluble fluoride by one of many methods found in the literature, have been found tedious and unsatisfactory (*23*, *27*). The technic is exacting. This method was used in the first studies reported by Smith, Lantz, and Smith (*19*).

The method of Fairchild (*9*) has been modified and used by Churchill (*7*), Hale (*11*), and Smith (*21*). This method calls for the addition of a ferric salt which forms ferric fluoride or the complex FeF_6^{---} with the fluorides present. The excess ferric ion is then caused to react with potassium iodide, and the liberated iodine is titrated with thiosulfate. The reliability of the method depends on the stability of the iron-fluoride complex and on a quantitative reaction between ferric iron and potassium iodide. The reaction

$$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$$

is reversible, and, if it is to be used in a quantitative determination, the iodide must be added in large excess (*25*). Fairchild and Churchill have not used sufficient potassium iodide. Upon testing the reliability of their methods, the present writers found that the amount of iodine liberated by the reaction of 5.0 cc. of approximately 0.08 *M* ferric chloride with the 10 cc. of 5 per cent potassium iodide in distilled water, according to their procedures, required an amount of 0.025 *N* thiosulfate which varied from 13.7 to 15.2 cc. Others (*6*) have noted similar variations in this reaction. Increasing quantities of potassium iodide (iodine-free) required increasing volumes of thiosulfate to react with the liberated iodine. Similar tests made by adding definite volumes (1

to 20 cc.) of standard sodium fluoride (0.84 gram per l.) to 100 cc. of distilled water gave discordant results. In these tests the difference between the amounts of thiosulfate used in the final titrations and those used in the blanks varied from −0.03 to +0.37 cc. per cc. of sodium fluoride (0.84 mg.) added. The average of twenty determinations was +0.25 cc. per cc. of sodium fluoride. Tests in which a constant amount of standard sodium fluoride was added and which were titrated in accordance with the procedures of Fairchild and Churchill varied as much as 1.0 cc. of 0.025 *N* thiosulfate. The presence of iron in waters to be analyzed for fluorides further complicates matters. Additional modification of these methods by Smith and Smith (*21*) has not improved their reliability. (A water from the Colorado River at Yuma, Ariz., which was reported by Smith to contain 4.0 p. p. m. of fluorides, but was not causing mottled teeth, was found by the present writers to contain only 0.4 p. p. m.) It is unfortunate that the Churchill method has been included in the appendix of the new Standard Methods of Water Analysis (*3*).

The method recently announced by Foster (*10*) calls for addition of excess ferric ion in order to obtain the ferric fluoride complex. The excess iron is determined by the thiocyanate method. Foster's data show no definite, constant relation between the ferric ion removed and the fluoride present. If the ferric fluoride or the FeF_6^{---} complexes were formed, 25 mg. of iron should remove 26 and 52 mg. of fluorides, respectively. The analytical data do not correspond with either of these complexes. One of the basic requirements of any quantitative method is that a constant and definite relation must exist between the reactants.

Thompson and Taylor (*24*) are using a modified Casares–De Boer method (colorimetric) for the determination of fluorides in sea waters. The procedure seems very empirical. Churchill (*7*) has proposed the use of a spectrograph for the determination of fluorides in waters. The method would undoubtedly be reliable but the cost of the apparatus would make its use prohibitive in most water laboratories.

Willard and Winter (*27*) have noted that soluble fluorides can be quantitatively distilled from acid solutions as hydrofluosilicic acid (H_2SiF_6). In this form and in the absence of large quantities of soluble salts (many interfere with direct determination), the fluorides can be determined by various methods. Allen and Furman (*1*, *2*) have investigated the use of cerous nitrate as a titrating agent and triphenyltin as a precipitant for soluble fluorides. Each method has certain distinct disadvantages. Wichmann and Dahle (*26*) have investigated a modified Steiger-Merwin method. This procedure depends on a bleaching, by the fluorides present, of the yellow color of peroxidized titanium salts. The present writers have not had very much success in determining the fluoride content of distillates by comparing the depth of yellow color developed in them with that developed in similar standard 50-cc. Nessler tubes containing various known quantities of sodium fluoride. The use of thorium nitrate as a volumetric precipitant as outlined by Willard and Winter (*27*) seems promising.

Recommended Method of Analysis

The present authors have found that, if waters containing small quantities of fluorides are made alkaline to phenolphthalein or litmus, they can be concentrated without loss of fluorine. This can best be accomplished by concentrating the sample in the distilling flask that is later to be used for volatilizing the hydrofluosilicic acid. Sufficient water should be concentrated so that the final volume of about 50 cc. will contain at least 0.2 mg. of fluorine. The following procedure is fundamentally that developed by Willard and Winter (*27*). It has been modified and adapted for use in the analysis of waters.

Reagents. (1) Zirconium nitrate, one gram of $Zr(NO_3)_4 \cdot 5H_2O$ in 250 cc. of water. (2) Alizarin red, one gram of sodium alizarin sulfonate in 100 cc. of ethyl alcohol. Filter off the undissolved residue and add 150 cc. of ethyl alcohol to the filtrate. Solutions 1 and 2 are kept in stock and mixed (three parts of 1 and two parts of 2) as needed. The color should be violet-red when mixed. (3) Thorium nitrate solution, 0.01 to 0.02 *N*, standardized against a standard fluoride solution. (4) Standard fluoride solution, lithium fluoride, 0.02 *N* (0.5188 gram/l.) or specially purified sodium fluoride (*1*), 0.02 *N* (0.8400 gram per l.). (5) Hydrochloric acid, about 0.2 *N*. (6) Sodium hydroxide solution, about 0.2 *N*.

Standardization of Thorium Nitrate Solution. Add small definite volumes of the 0.02 *N* fluoride solution from a buret to a small tall-form beaker or Erlenmeyer flask, add water to make the volume approximately 20 cc., and then add an equal volume of ethyl alcohol. Add six drops (about 0.15 cc.) of the zirconium-alizarin mixture, then only enough dilute hydrochloric acid to destroy the color. Avoid excess acid. The present writers have confirmed the findings of Armstrong (*4*)—namely, that it is better to use only the sodium alizarin sulfonate as the indicator, instead of the zirconium-dye mixture, in titrating solutions containing less than 0.5 mg. of fluorides. Using the thorium nitrate solution, titrate over a white surface (in good light) to a faint permanent reappearance of color. Titrate slowly upon nearing the end point. Run a blank titration on the indicator by determining the volume of standard (0.02 *N*) fluoride solution necessary to cause disappearance of color in a slightly acid water-alcohol solution of six drops of the indicator mixture and compare this with the volume of standard thorium nitrate necessary to discharge the color. Calculate the strength of the thorium nitrate solution by use of the following equation:

$$1.0 \text{ cc. } Th(NO_3)_4 = \frac{\text{cc. of } 0.02\ N\ F^- \text{ soln.}}{\text{cc. of } Th(NO_3)_4 \text{ soln.}} \times 0.38 = A \text{ mg. of } F^-$$

Analytical Procedure. Make the water to be examined alkaline to litmus or phenolphthalein and concentrate a definite volume (to contain at least 0.2 mg. of fluorine) to approximately 50 cc. in a 250- or 500-cc. distilling flask. Add a few glass beads or silica, 20 cc. of concentrated sulfuric acid (60 per cent perchloric acid may be used) and sufficient water to cause the solution to boil at 110° C. Place the flask on an asbestos mat with an opening sufficiently large for about one-third of the flask to be exposed to the flame. Close with a two-hole rubber stopper through which passes a thermometer and capillary tube, both of which extend into the liquid. Connect a dropping funnel with the capillary tube so that water may be added during the process of distillation. Connect the flask with a water condenser. The distillate may be collected in an open container. Distill until the boiling point reaches 130° to 140° C. and hold at approximately this temperature by adding water through the capillary tube until all the fluoride has been volatilized. This is usually accomplished by collecting 50 to 75 cc. of distillate, but the present writers prefer to collect about 100 to 150 cc. and then concentrate this to approximately 20 cc. on a hot plate after it has been made alkaline. Neutralize most of the alkali before proceeding. Add the six drops of indicator, dilute acid until the color of the indicator just disappears, and then an equal volume of neutral alcohol. Be sure the solution is only faintly acid. If no fluorides are present, the color will not be discharged. Redistill if a precipitate forms. Titrate at once in a tall-form beaker with the standardized thorium nitrate solution to the faint reappearance of the pink color. Report as parts per million of fluorides.

Titration of known quantities of fluorides with the thorium nitrate standard always gave a definite and constant relation between the two. In order to check further the above recommended procedure, the authors prepared a stock synthetic water which contained the following c. p. reagents:

	P. p. m.		*P. p. m.*
$CaCO_3$, as $Ca(HCO_3)_2$	170	$FeCl_3$	1.0
$MgSO_4$	150	NH_4Cl	3.0
NaCl	30		

To one-liter samples of this water were added various but known quantities of fluorides (0.5 to 5.0 p. p. m. as sodium fluoride). These samples were then concentrated and ana-

lyzed in accordance with the above recommended procedure. The analyses checked within +0.10 to −0.10 p. p. m. of the amount of fluorides added. Duplicate analyses were also made of most of the natural waters examined; these also checked within satisfactory limits. The accuracy of the method, therefore, seems to fall within the limits of the periodic variations noted in the chemical make-up of natural waters.

The residue from waters containing in the order of 1000 p. p. m. of chloride should be distilled into sufficient alkali in order to keep the distillate from becoming too acidic. If abnormal quantities of aluminum salts, gelatinous silica, or borates are present in a water, a larger volume (about 200 cc.) of distillate should be collected in order to guarantee complete recovery of the fluorides present.

A number of Illinois waters (untreated) have been examined for fluorides. Four lake-reservoir samples contained from 0 to 0.5 p. p. m. Five river samples contained from 0.2 to 0.5 p. p. m. Five shallow-drift, gravel, and limestone wells, distributed about the state, contained up to 0.7 p. p. m. of fluorides. One 497-foot limestone well in north central Illinois produces a highly mineralized water containing 1.1 p. p. m. of fluorides. Five deep St. Peter wells in and around this same district produce highly mineralized waters containing from 1.0 to 2.0 p. p. m. of fluorides. One 404-foot Niagaran well in this same district produces water containing 3.7 p. p. m. of fluorides. Drainage from a fluospar mine contained 1.7 p. p. m. of fluorides, while a 100-foot well nearby contained only 0.1 p. p. m.

Dean (*8*) has reported that some of the Monmouth residents are affected with slight mottling of the teeth and that 53 per cent of the children in Minonk and 66 per cent of those in Fairbury have mottled teeth. Others (*8*) have reported mottled enamel in Milan and in and around Emington and Kempton. All of these waters have been found to contain 1.0 p. p. m. or more of fluorides.

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Sources of Error in the Use in Water Analysis of Fairchild's Method for Determination of Fluoride in Phosphate Rock

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The method developed by Fairchild (*2*) for the determination of fluoride in phosphate rock has been used for the determination of fluoride in water (*1*, *3*).

Studies of this method have shown that (1) with no interfering elements present the method usually gives high results and is accurate only to 0.2 to 0.4 mg. of fluoride, less than many waters contain in a liter, and (2) sulfate apparently withdraws some of the iron from reaction with potassium iodide and gives the same effect as fluoride. The amount withdrawn depends to some extent on the amount of sulfate present and to some extent on whether the sulfate is present as the sodium, calcium, or magnesium salt. The effect of sulfate may be practically eliminated by making the sample just acid to methyl orange, adding the 2.2 cc. of *N* hydrochloric acid which is usually added later, precipitating the sulfate with barium chloride (which has no effect on the method) and proceeding as before, but omitting further addition of acid.

Chloride if present as the sodium salt does not appreciably affect the result. One gram of calcium or magnesium chloride tends to give a slightly high result, giving an apparent fluoride of 0.3 mg. when none is present. Nitrates and borates, in amounts usually found in water, do not interfere.

If small volumes of water are used for the determination, the possible error as indicated by the range in readings of the controls might be as great as the fluoride present or even greater. Large volumes, if used, would necessitate, in many waters, the removal of sulfate and concentration, with the probability of precipitation of calcium fluoride. The method does not seem well adapted to the determination of fluoride in water.

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Losses of Volatile Matter in Coal by Standard Method

Water of Hydration and Carbon Dioxide of Mineral Matter

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WATER of hydration and carbon dioxide occurring in the mineral matter of coal are disturbing factors in coal analysis. They have been given considerable study by coal chemists, especially in connection with the use of analyses for purposes of coal classification (*2*, *3*), as here it is desirable to know the composition of the pure coal substance—that is, of the coal free from its ash-forming minerals. If proximate analyses are used as a basis for coal classification, the determination of volatile matter becomes important. Parr (*5*) proposed a system of coal classification based on volatile matter and B. t. u. of coal free of mineral matter. He applied corrections to the volatile matter as determined on the assumption that this volatile matter includes as a noncoal constituent the water of hydration of the shaley constituent of the ash-forming mineral matter.

The tests described herein were made to determine whether the water of hydration and the carbon dioxide of the mineral matter occurring in coal are driven off in the standard method for determination of volatile matter (*1*). In this determination the coal is heated for 7 minutes in a furnace maintained at a temperature of 950° C.

The principal source of carbon dioxide in coal is calcite. As carbon dioxide is not usually determined in coal analysis, there is not much information as to its amount in various coals. Parr (*6*) determined carbon dioxide in about four hundred coals of Illinois and found that approximately 9 per cent of these coals contained less than 0.1 per cent of carbon dioxide; nearly 50 per cent of the coals showed carbon dioxide in excess of 0.5 per cent; 20 per cent more than 1.0 per cent of carbon dioxide; and 3 per cent over 2 per cent of carbon dioxide. The highest content of carbon dioxide found in these coals was 4.4 per cent. Fish and Addlestone (*4*) analyzed samples of coal from ten Virginia coal beds and found carbon dioxide ranging from 0.03 to 1.41 per cent. They also analyzed twenty-eight samples of coal from the Merrimac bed of Virginia and found from 0.26 to 5.4 per cent of carbon dioxide. Unpublished analyses of eighty-five coals from various parts of the United States, made at the Pittsburgh Experiment Station of the U. S. Bureau of Mines, show carbon dioxide ranging from 0.0 to 2.38 per cent, with an average of 0.53 per cent.

Experimental Data

A number of minerals containing water of hydration were selected for test. They were pulverized to pass a 60-mesh sieve, and a 1-gram sample was placed in a 10-cc. platinum crucible provided with a capsule cover. The crucible and contents were heated in an electric volatile-matter furnace for 7 minutes at 950° C. These conditions are the same as those used for the standard determination of volatile matter in coal. The loss in weight was compared to the loss obtained on igniting the minerals to constant weight in a muffle furnace. A number of the minerals were also analyzed for moisture, and the water of hydration was determined by the Penfield-tube method. Table I shows the results of these tests.

A comparison of the losses in weight as determined in the volatile-matter furnace with the ignition losses to constant weight shows that the water of hydration was completely removed for all minerals tested with the exception of zoisite. This mineral showed a loss of 4.51 per cent on heating to constant weight at 950° C. As the zoisite specimen contained 2.72 per cent carbon dioxide, the ignition loss of 4.51 per cent includes carbon dioxide and water of hydration. The loss on heating the zoisite in the volatile-matter furnace for 7 minutes at 950° C. was 3.41 per cent, showing that all of the volatile constituents were not driven off. A determination of water of hydration by the Penfield-tube method of the mineral after the 7-minute ignition in the volatile-matter furnace showed that 0.97 per cent of the water of hydration remained in the sample, and as the original sample had 1.76 per cent water of hydration it is apparent that this water was only partly removed by heating for 7 minutes at 950° C. The sample of allanite contained ferrous iron which oxidized on ignition and the increase in weight due to oxidation accounts for the figures for the ignition losses being lower than the water actually determined in the sample. All the water of hydration of this mineral was driven off on heating for 7 minutes at 950° C. It appears safe to assume from these tests that the water of hydration of the mineral matter

Table I. Loss of Water of Hydration of Various Minerals Heated in Standard Volatile-Matter Furnace

Mineral	Nature of Impurities	Moisture at 105° C.	Water of Hydration	Total Water	Ignition Loss to Constant Weight 750° C.	Ignition Loss to Constant Weight 950° C.	Loss in Volatile-Matter Furnace, 7 Minutes at 950° C.
		%	%	%	%	%	%
Fireclay	CO_2, none; sulfides, present	1.11	8.70	9.81	10.58	[a]	10.64
Kaolin	CO_2, none; sulfides, none	0.45	13.12	13.57	13.76	[a]	13.89
Kaolin	CO_2, none; sulfides, none	1.73	12.90	14.63	14.76	[a]	14.94
Micaceous sandstone	CO_2, none; sulfides, present	0.20	3.24	3.44	3.28	[a]	3.36
Muscovite	CO_2, none	0.88	4.93	5.81	6.33	[a]	6.44
Muscovite	CO_2, none; sulfides, present	[a]	[a]	[a]	3.75	[a]	3.92
Biotite	CO_2, none	0.56	1.10	1.66	1.68	[a]	1.75
Serpentine	CO_2, none	[a]	[a]	[a]	14.06	[a]	14.24
Serpentine	CO_2 present as calcium and magnesium carbonate	[a]	[a]	[a]	14.85	[a]	15.19
Prochlorite	CO_2, small amount	[a]	[a]	[a]	10.10	[a]	10.23
Allanite	Ferrous iron, present; CO_2, none; sulfides, none	0.77	4.24	5.01	3.67	3.70	4.63
Epidote	CO_2, none; sulfides, none	0.10	1.91	2.01	1.07	2.24	2.24
Zoisite	CO_2, 2.72 per cent	0.05	1.76	1.81	2.70	4.51	3.41

[a] Not determined.

Table II. Loss of Carbon Dioxide for Calcite Minerals Heated in Standard Volatile-Matter Furnace

Mineral	Nature of Impurities	Ignition Loss[a] to Constant Weight	Loss in Volatile-Matter Furnace: 7 Min., 950° C.	10 Min., 950° C.	15 Min., 950° C.	7 Min., 1000° C.	10 Min., 1000° C.
		%	%	%	%	%	%
Calcite (ordinary)	Not determined	42.77	33.3	36.4	42.3	41.0	42.8
Calcite (Iceland spar)	Not determined	43.67	28.9	32.7	42.9	40.2	43.9
Calcite (limestone)	SiO_2, 0.1; Al_2O_3, 0.1 Fe_2O_3, 0.4; MgO, 0.9	43.56	32.5	38.3	43.4	41.0	43.9

[a] Ignition loss determined by heating in a muffle furnace to constant weight at approximately 900° C.

in coal is completely driven off with the volatile matter of the coal substance when volatile matter is determined by the standard method, with the exception of minerals such as zoisite which require intense ignition for complete removal of water of hydration.

Three minerals which are essentially calcium carbonate were tested for loss of carbon dioxide when subjected to the standard method used for volatile matter in coal. All the carbon dioxide was not driven off from these minerals when heated in the volatile-matter furnace for 7 minutes at 950° C., so additional tests were made by heating for 10 and 15 minutes at 950° C., and for 7 and 10 minutes at 1000° C. Table II shows the results of these tests.

The calcite minerals gave erratic results in individual determinations when heated at 950° C. The figures shown in the table for these values are the averages of a number of determinations. Seven determinations were made for the ordinary calcite; the individual determinations ranged from 30.4 to 36.6 per cent, with an average of 33.3 per cent. Six determinations were made for the Iceland spar; these ranged from 27.1 to 30.7 per cent, with an average of 28.9. In case of the limestone six determinations were made; these ranged from 28.5 to 35.5, with an average of 32.5 per cent. The table shows that heating for 10 minutes at 950° C. does not remove all the carbon dioxide and that it is removed completely by heating for 15 minutes at this temperature. At a temperature of 1000° C. the carbon dioxide is not completely removed when heated for 7 minutes but it is all removed by heating for 10 minutes.

A sample of dolomite (calcium magnesium carbonate) was also used in the tests but is not included in Table II. This mineral when heated for 7 minutes at 950° C. decomposed so rapidly that there was considerable mechanical loss of mineral particles, as evidenced by particles being ejected from the crucible and collecting on top of the crucible lid. On account of this mechanical loss of particles the loss in weight in the volatile-matter furnace was higher by approximately 2 per cent than the loss on slow ignition in a muffle furnace, which latter indicated a carbon dioxide content of 47.4 per cent.

A sufficient amount of the limestone was added to a Pittsburgh-bed coal to give a carbon dioxide content of approximately 5 per cent. The exact amount of carbon dioxide was determined by analysis. This mixture was then run for volatile matter by the standard method used in coal analysis—that is, by heating 1-gram samples for 7 minutes at 950° C. The residual carbon dioxide remaining in the residue from the volatile matter determination was determined by analysis. The results showed that approximately 70 per cent of the carbon dioxide was expelled with the volatile matter of the coal.

The standard method for determination of volatile matter in coal specifies that the sample shall be heated for 7 minutes at a temperature of 950° C. ± 20° C. According to this specification the temperature may range from 930° to 970° C. Tests made on coal have shown that this variation in temperature will not cause any significant difference in the determination of volatile matter of the coal substance. Tests were made by heating 1-gram samples of the limestone for 7 minutes at different temperatures varying from 930° to 970° C. Table III gives the results of these tests, and shows a wide range in the carbon dioxide evolved at this range of furnace temperatures, as 19.9 per cent of carbon dioxide was driven off at 930° C. and 34.6 per cent at 970° C. These are average values and the table shows that the individual determinations differed considerably. Assuming that the ignition loss of 43.56 shown in Table II consists of the carbon dioxide present, Table III shows that 45.7 per cent of the carbon dioxide present was removed at 930° C. and 79.4 per cent at 970° C. The relatively large differences in the individual determinations at 950° C. were probably caused by small unavoidable differences in the furnace temperature, although this was maintained as uniform as possible with the standard furnace used for this determination.

Table III. Loss of Carbon Dioxide Obtained by Heating Limestone for 7 Minutes in Volatile-Matter Furnace

Temperature	Individual Determinations	Average	Average CO_2 Removed
° C.	%	%	%
930	22.1, 18.7, 18.8	19.9	45.7
940	25.0, 24.7 24.7, 25.3	24.9	57.2
950	28.5, 28.8 35.1, 34.0 35.5, 33.0	32.5	74.6
970	34.5, 35.6, 33.7	34.6	79.4

Because of the incomplete removal of carbon dioxide from calcite and the erratic results obtained over the temperature range of 930° to 970° C., it does not appear feasible to apply corrections to the volatile-matter determination for carbon dioxide from calcite, in coals containing relatively large amounts of mineral carbonates. With such coals it would be better practice to remove the major portion of the calcite previous to analysis by means of a float-and-sink method.

The ignition losses shown in Table II were made by heating 1-gram samples to constant weight in a muffle maintained at a temperature of 900° C. The standard method for determination of ash in coal (*1*) specifies heating 1-gram samples of coal to constant weight (±0.001 gram) at a temperature between 700° and 750° C. Tests made by heating the three calcite minerals under these conditions show that all the carbon dioxide is removed in from 2 to 2.5 hours. These results checked closely with the loss on ignition at 900° C. as given in Table II. It is safe to conclude that all carbonates are decomposed in the standard method for determination of ash in coal.

Reference to Table I shows that approximately one-half of the water of hydration was removed by heating epidote to constant weight at 750° C. The sample of zoisite gave a loss under these conditions of heating equivalent to the amount of carbon dioxide present as an impurity in the mineral. Analysis of this mineral after heating to constant weight at 750° C. showed that the carbon dioxide was completely removed, but that little, if any, of the water of hydration had been removed, as a Penfield-tube test on the ignited material showed 1.54 per cent water of hydration as compared to 1.76 per cent for the original sample. These tests

show that minerals such as epidote and zoisite require intense ignition for complete removal of water of hydration and that this water is not removed in the standard method for determination of ash in coal by which the coal is ignited to constant weight at a temperature between 700° and 750° C. No information is available as to the amount of such minerals that may be present in coal.

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Determination of Small Amounts of Manganese in Salt Solutions

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SINCE the introduction in 1917 by Willard and Greathouse (*9*) of potassium periodate for the oxidation of manganese to permanganate, the method has come into general use. The color from 0.01 mg. of manganese in 50 cc. has been reported as easily checked against known standards. Recently a still more delicate color reaction has been suggested by Stratton, Ficklen, and Hough (*8*) using benzidine hydrochloride, with an optimum concentration for color comparison between 0.001 and 0.0001 mg. per 100 cc. Both methods have been used in these laboratories for the determination of traces of manganese in salt solutions.

POTASSIUM PERIODATE METHOD

The potassium periodate method depends upon the oxidation of the manganese in acid solution to the colored manganese ion, and comparison with a standard similarly prepared. Willard and Greathouse, for 100 cc. of solution containing 2.5 or more mg. of manganese, advised 10 to 15 cc. of concentrated sulfuric acid, 20 cc. of concentrated nitric acid, 5 to 10 cc. of 85 per cent phosphoric acid, or mixtures of two or more acids. The amount of acid was shown to vary widely without influencing the results. This method was used by Bartow and Thompson (*1*) without the sulfuric acid, for manganese in potable waters.

In 1930 Richards (*6*) reported results on biological material that showed the desirability of controlling the acidity very accurately in order to get satisfactory results with small quantities of manganese. Sulfuric acid was used and, with the acidity from 5 to 6 per cent, no fading of the color was observed. Excess acidity prevented development of the full color or caused it to fade rapidly. In the same year Skinner and Peterson (*7*) published a paper on the determination of manganese in animal tissue. They showed that 10 to 20 grams of material, when ashed in a muffle furnace at cherry red, could be extracted with 5 cc. of 85 per cent phosphoric acid and 30 to 50 cc. of water and, after filtering, could be oxidized directly with 0.3 gram of potassium periodate without loss of color. They found that 0.01 mg. of manganese in 50 cc. gave a readable color when compared in Nessler tubes against an inverted V of white paper.

In these laboratories it became necessary to know the content of manganese fairly accurately in a number of salt solutions both separated and together, and in concentrated and dilute solutions. The salts in which the manganese was determined included potassium nitrate, primary calcium phosphate, magnesium sulfate, ferric chloride, and later ferric citrate. In all cases 50-cc. Nessler tubes were used for the color comparison. The tubes were carefully matched for color of glass; for this reaction, tubes with a trace of brown in their composition were found to be less delicate than others. With a good frame and milk-glass reflector, and with sky light, the comparison was as easily made as with the inverted V paper used by Skinner and Peterson. It was usually possible to detect the presence of 0.001 mg. of manganese in the 50-cc. tube; 0.002 mg. could always be seen, and there was a distinct difference in additions of 0.001 mg. Colors produced by the potassium periodate oxidation were remarkably stable; in some cases standard solutions which had been kept for 7 months in the dark showed no trace of fading.

The standard solution was made from potassium permanganate of known normality, or from recrystallized potassium permanganate as suggested by Richards (*6*). In both cases the solutions were reduced by sodium sulfite and sulfuric acid, and the sulfur dioxide boiled off. Various combinations of sulfuric, nitric, and phosphoric acids for the oxidation with potassium periodate showed that phosphoric acid alone was the most satisfactory. The remainder of the oxidations were made in 50 to 100 cc. of a solution containing 5 cc. of 85 per cent phosphoric acid and 0.3 gram of potassium periodate. A few minutes' boiling usually brought out the full color; the solution was then cooled and made up to 50 cc. in the Nessler tubes. A further solution was made up from the same standards and reduced with the sulfur dioxide as before, or by Bureau of Standards sodium oxalate, diluted until the content was 0.002 mg. of manganese per cc. and, when freshly oxidized by potassium periodate, used as a check on the diluted standard solutions. A few cubic centimeters of this (solution B+), before oxidation, were used with separate samples of unknowns to test for interfering substances.

A liter of the distilled water used was evaporated to 50 cc., but showed no trace of manganese after oxidation. By varying the amounts of potassium periodate, this salt also was shown to contain no manganese. Samples of commercial 85 per cent phosphoric acid contained from 0.002 to 0.003 mg. in 5 cc. By recrystallizing this could be elimi-

nated, but usually a fresh bottle was checked and the correction made.

A dilute solution of the previously mentioned recrystallized salts was tested for its manganese content. This solution contained per liter 0.6 mg. of iron (as ferric chloride), 16 mg. of calcium, 24 mg. of manganese, and 312 mg. of potassium. The result, along with a check on the water, is shown in Table I. After subtracting the 0.002 mg. of manganese in the 5 cc. of phosphoric acid, it will be seen that no manganese can be detected at this dilution.

A solution of the same salts was then made up 200 times as concentrated. Some precipitation which occurred at this concentration was removed by filtration or centrifuging. Checks were made by addition of solution B before and after precipitation to determine any possible loss or interference. The volume was made small before the removal of the precipitate, and the oxidation with the potassium periodate was carried out in a more dilute solution. The oxidation in some cases caused further precipitation; Skinner and Peterson (*7*) recommend filtration and reoxidation, or allowing the precipitate to settle in the Nessler tube and transferring the supernatant liquid to a second tube. The solution evidently contains 0.006 mg. of manganese in 100 cc.

Table I. Manganese in Mixed Salt Solutions

Manganese Added as Solution B	Manganese Found: In 50 cc. water + 5 cc. H_3PO_4	In 50 cc. dilute solution + 5 cc. H_3PO_4	In 100 cc. concentrated solution + 5 cc. H_3PO_4
Mg.	*Mg.*	*Mg.*	*Mg.*
0	0.002	0.002	0.008
0.002	...	0.004	...
0.004	...	...	0.012
0.008	0.010	0.009	...

The separate salts were then made up in the same dilution as the concentrated solution in Table I. Table II shows the figures. The total manganese in the separate salts checks very closely the amount found when determined in the concentrated solution. Six recrystallizations subsequently removed all trace of manganese from the magnesium sulfate.

Table II. Manganese in Separate Salt Solutions

Manganese Added as Solution B	Manganese Found in 100 cc. Solution with 5 cc. H_3PO_4: Water	$FeCl_3$	$Ca(H_2PO_4)_2$	$MgSO_4$	KNO_3
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0	0.002	0.003	0.002	0.008	0.001+
0.002	...	0.005	0.004	...	0.004

Ferric citrate has been used as a source of iron both for plants and for animals, and it became desirable to know the amount of manganese in the commercial product and whether reprecipitation would decrease it. The citrate, however, interfered with the oxidation, as no color was produced on adding solution B and heating with phosphoric acid and potassium periodate. Willard and Greathouse suggested boiling with nitric acid to free from reducing agents, adding persulfate if carbon was present. Skinner and Peterson ashed their samples in a muffle furnace. In this case it was sufficient to heat the iron citrate in porcelain crucibles until the carbon was removed and the ferric oxide formed. Several methods were checked for taking up the residue; 0.1 gram of the finely ground, ashed citrate, digested for several hours on the water bath with 50 cc. of water and 5 cc. of 85 per cent phosphoric acid, usually gave a solution which could be satisfactorily oxidized with potassium periodate.

Ferric citrate has not been obtained in crystalline form. The solution can be concentrated to a sirup and precipitated as a yellow amorphous mass by the addition of ethyl alcohol. If this precipitate is dissolved in water, and the solution allowed to evaporate to dryness in thin layers, red-brown laminas are obtained which are slowly soluble in water. These laminas were treated in the same way as the crude ferric citrate, but the manganese content increased slightly rather than decreased.

A citrate solution supplied by H. L. Keil showed much less manganese. This had been made from iron wire precipitated as ferric hydroxide, with recrystallized citric acid. The solution was copper-free and contained 1.21 mg. of iron per cc. Five cubic centimeters of this were evaporated to dryness in a double crucible with a few drops of nitric acid, then heated to redness and treated in the same way as before. The solution was found to contain 0.0002 mg. of manganese per cc. The ferric citrate results are shown in Table III.

Table III. Manganese in Ferric Citrate

Manganese Added as Solution B	Manganese Found in 50 cc. Solution + 5 cc. H_3PO_4: Water	0.1 gram crude iron citrate	0.1 gram precipitated iron citrate	5 cc. Keil's solution
Mg.	*Mg.*	*Mg.*	*Mg.*	*Mg.*
0	0.002	0.100	0.110	0.003
0.002	...	...	...	0.005

Benzidine Method

The benzidine reaction with manganese was investigated by Feigl (*2*), who used it as a colorimetric method for the detection of the presence of that element. Feigl showed that the intense blue color was also given by other oxidizing elements—e. g., titanium, cerium, and bromine. When manganous sulfate was boiled with alkali and filtered, and the precipitate on the filter touched with a drop of benzidine in acetic solution, the blue color which appeared was usually stable, although with small amounts it soon faded. The reaction was sensitive under the best conditions to 1 in 125 million, and was explained as the result of an autoxidation in which the manganese participated. The reaction was adapted to microtechnic (*3*).

Olszewski (*4*) applied the method to the qualitative determination of manganese in drinking water, and preferred an acetic acid solution of the benzidine to a hydrochloric solution. He did not advise the reaction as a quantitative method, but recommended instead the persulfate oxidation. Olszewski also investigated the reaction of free chlorine with benzidine chloride and used the blue color produced in solution for a semiquantitative determination of the chlorine in drinking water (*5*). He showed that this reaction was influenced by the presence of carbonates and organic matter, by the quantity of the benzidine chloride added, and to some extent by the pH. He states that in a solution containing free chlorine and small amounts of manganese, the blue-green color due to the manganese can be avoided by shaking the solution at once, to prevent the acid in the reagent from reacting with the manganese.

Stratton, Ficklen, and Hough (*8*) find that if benzidine chloride is added to a very dilute solution containing the permanganate ion, a brilliant blue-green color is produced which is more favorable for colorimetric estimation than the natural color of the permanganate ion. They recommend 2.3 grams of benzidine base in 100 cc. of 5 per cent hydrochloric acid. One drop of this reagent, added to 100 cc. of a solution containing from 0.001 to 0.0001 mg. of permanganate ion, gives a blue-green color which can be matched against a known standard. In contrast to the remarkable permanency of the permanganate color produced by potassium periodate, the blue fades rapidly; Stratton therefore suggested a permanent standard made from copper sulfate and picric acid.

In solutions containing small amounts of manganese, the speed with which the color fades made it difficult to obtain quantitative results. The reaction was therefore examined further. Commercial benzidine base was recrystallized

from water or benzene and dissolved to saturation in different concentrations of hydrochloric, nitric, acetic, citric, and other acids. When manganese sulfate was boiled with sodium hydroxide as described by Feigl, the precipitate after filtering gave a blue color with a few drops of all the benzidine solutions, except with high acidities. A solution of commercial benzidine hydrochloride (powder) in water produced a blue which in general was more lasting than one from a saturated solution of benzidine in 5 per cent acetic acid. With very small amounts of manganese, the color from any combination faded.

A 50-cc. solution containing 0.025 mg. of manganese as manganese sulfate (approximately 1 in 2 million) was boiled with 2.5 cc. of 0.1 *N* sodium hydroxide. The brown precipitate on the filter, with one drop of the benzidine acetate solution, showed a strong blue which faded only after several hours; with one drop of the chloride the blue was similar in color, but there was no fading even after several days. When the amount of manganese was reduced to 0.0025 mg. before boiling with the alkali, no brown precipitate could be seen on the filter paper, but both acetate and chloride produced traces of blue which faded gradually. The blue from the acetate solution seemed somewhat the brighter.

The precipitate was also obtained by treating 100 cc. of a solution containing 0.3 gram of recrystallized potassium permanganate with 33.5 cc. of a diluted (1 to 1) 3 per cent hydrogen peroxide. The colloidal solution of manganese dioxide so produced was stable and could be diluted without causing immediate precipitation. Five cubic centimeters of this colloidal solution before dilution, when passed through a filter paper, left sufficient precipitate on the filter to give a blue color with one drop of the benzidine acetate or chloride. On diluting, 5 cc. containing approximately 0.0016 mg. of manganese failed to give any color on the filter paper; when this amount was boiled with 1 cc. of 0.1 *N* sodium hydroxide, cooled, and filtered, the filter paper again showed blue with a drop of the acetate. This is about 1 in 3 million. The same quantity of manganese, when diluted to 1 in 100 million or 1 in 200 million before heating with sodium hydroxide, gave a similar color on the filter paper. The limiting factor in this case seemed to be the quantity of manganese and not the dilution. The test failed with 0.0016 mg. of manganese as manganese sulfate when the solution was boiled with alkali at dilutions from 1 in 100 to 1 in 200 million, although the same amount gave a clear blue coloration at 1 in 3 million. Evidently it is the dilution factor which causes the failure. Any adaptation to a quantitative determination by this method did not seem feasible.

Solutions of manganese sulfate, boiled with sodium hydroxide and made neutral to methyl orange but not filtered, showed the blue color with both the chloride and acetate of benzidine; the color was stable only if a precipitate formed. With 0.025 mg. of manganese at a concentration of 1 in 200,000, with one drop of the saturated benzidine hydrochloride, a bright blue precipitate was produced which was comparatively stable. At a concentration of 1 in 400,000 there was a fine pale blue precipitate formed which was stable for some hours. At higher dilutions a light blue color appeared in the solution but began to fade at once. A change in the pH value of the solution did not stop the disappearance of the color.

Solutions of potassium permanganate gave almost the same results. At a dilution of 1 to 100,000 for the manganese, a solution containing 0.05 mg. gave the blue color with 1 drop of the benzidine hydrochloride. This gradually faded and a slight brown precipitate was produced. With 0.005 mg. of manganese at a dilution of 1 to 1 million the deep blue color faded gradually. At increasing dilution the color produced was successively lighter and faded more quickly.

An attempt was made to stabilize the intense blue color of the higher concentrations by shaking with various organic solvents, such as ether, chloroform, etc., but without success. However, at a concentration of 1 to 100,000, the addition of a salt to the solution, either before or just after the benzidine chloride was added, caused the formation of a deep blue flocculent precipitate. This precipitate was quite stable when left in the solution or when filtered out. At 1 to 1 million (0.005 mg. of manganese) no precipitate was formed, but the blue of the solution was the same color as the precipitate at the higher concentration, and this blue was also stable for many hours. Potassium nitrate was particularly good, but ammonium chloride, magnesium chloride, ammonium nitrate, and others produced the same effect. More salt was needed at the higher dilution—about 0.5 gram in 5 cc. At still higher dilutions the addition of the salt failed to prevent the fading, and when the precipitate from the 1 to 100,000 was diluted to 1 to 20 million the color disappeared in a few minutes.

Unless some method can be found to prevent this quick change of color in the dilute solutions, the benzidine hydrochloride or acetate test for manganese, while useful in qualitative analysis (*3*, *4*), will be of value only under very special conditions for a quantitative determination.

Summary

Oxidation of manganese in mixed salt solutions, with potassium periodate in phosphoric acid, has given good colorimetric comparisons; a difference of 0.001 mg. of manganese in 50-cc. Nessler tubes can be observed.

The blue color formed by manganese with benzidine, recommended by Feigl and Olszewski for qualitative analysis of manganese, and as a quantitative method by Stratton, Ficklen, and Hough, has been investigated. The deep blue color can be stabilized both as a precipitate and in solution with a concentration around 1 in 1 million, with the amount of manganese from a few hundredths to thousandths of a milligram. At very dilute concentrations the color is much lighter and fades rapidly. No way was found to prevent this fading, and the loss of color interferes greatly with the use of the method for quantitative determinations.

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Forgeries Detected by Chemical Test. Siegfried Türkel, research chemist for the police administration of Vienna, and associates have recently revealed chemical methods of detecting writing ink in places where it does not belong. The Vienna experts observed that all writing inks contain chlorides, but in widely variant quantity. The chloride slowly spreads in paper, though being colorless is invisible to the human eye. Doctor Türkel, by a simple chemical reaction, replaces the chloride in a document by metallic silver, deposited as a black image like that of a kodak print. In the same operation he bleaches out the normal ink dye. The document, photographed to yield a "chloride print," takes on a new appearance, depending on its age: one hour old, clear black writing; one day, clear but with broadened lines; four days, margin of pen stroke hazy; ten days, quite fuzzy; sixty days, small loops in letters filled up; six months, small writing illegible; one to two years, entirely illegible. With certain inks the chloride spreads so effectively that the actual pen-stroke line is largely freed of that substance. In such a case white lines will be seen on a fuzzy black background when the silver treatment is given. The tell-tale spreading of chloride is caused by the slight condensation of moisture from the air upon the paper fibers.

Stability of Fats and Oils

Applications of the Methylene Blue Test

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Recent developments in rancidity and stability tests are reviewed, and additional data on the use of methylene blue as an oxidation-reduction indicator are presented. Photoelectric control of the end point has not been found satisfactory in testing hydrogenated fats, because of secondary color changes that take place in the reaction mixture. Stability curves for a number of shortening products and salad oils are given. Light has been used to shorten the induction period in the accelerated peroxide test, and the relation of methylene blue fading time to Kreis values and peroxide values has been determined for cottonseed oil aged to a peroxide value of 250 millimoles.

THE relationship between oxidative induction period and the fading time of methylene blue in oils exposed to radiation was first pointed out by Greenbank and Holm (*4*), who made it the basis of a photoelectric stability test. The possibilities of adapting the method to routine keeping-quality determinations were outlined in a previous paper (*12*) from this laboratory, including a description of a modified apparatus. Since that time extended use of the method on a variety of fats has led to a better understanding of its limitations, which, while not detracting from the value of the method for certain applications, necessitated further changes in the apparatus. Also the use of accelerated oxidation data to supplement individual fading-time determinations will be pointed out, in conjunction with comparative figures on peroxide formation.

The increasing attention being centered on the development of improved stability test and evaluation of fat stabilizers becomes apparent in reviewing recent literature. Of especial interest in connection with the methylene blue method is the procedure recommended by Bruere and Fourmont (*3*), involving the use of a series of decolorized reduction indicators having graded reduction potentials. Depending on the stage of incipient rancidity in the fat under examination, certain of the indicators revert to the colored form. Probably a comparison of results by this method with the iodometric peroxide estimations of Lea (*8*) or Wheeler (*13*) would show that the color change depends upon the presence of peroxides in the sample.

The limitations of the Kreis test applied to fats stored in hermetically sealed containers have been pointed out by Pool (*10*), who uses oxygen absorption to supplement this test. Richardson, Eckey, and Andrews (*11*) also employ oxygen absorption measurements to establish the stability of salad oils supplied to the mayonnaise industry. Grettie and Newton (*6*) have combined certain features of the Bailey (*2*) and the Issoglio (*7*) tests to arrive at a method for following oxidative decomposition under accelerated aging conditions. More recently, Newton (*9*) has used the rate of peroxide formation to measure the antioxidant effect of carotinoid pigments.

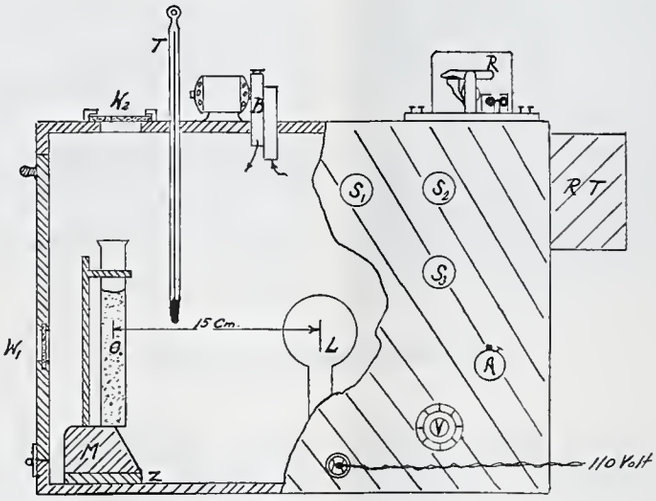

Figure 1. Apparatus for the Estimation of Fat Stability by the Methylene Blue–Light Reaction

A.	Bimetallic thermoregulator	*RT.*	Rectifier transformer
B.	Heater-blower	S_1.	Resistance in relay circuit
M.	Magnesia block	S_2.	Resistance in heater circuit
O.	Oil color tube containing sample	S_3.	Resistance in blower circuit
L.	100-watt daylight lamp	*V.*	Adjustable ventilator
R.	Mercury relay	W_1, W_2.	Windows
T.	Thermometer	*Z.*	Drawer slide

Experimental

Apparatus. The assembly previously described (*12*) has been simplified by omission of the photoelectric control, so that the unit may be constructed at low cost in any laboratory having average facilities. Figure 1 presents the arrangement of the essential parts of the apparatus now in use.

The reaction chamber is an air thermostat of asbestos-lined wood construction 10 × 10 × 14 feet long. The sliding sample rack *Z* holds six American Oil Chemists' Society oil color tubes *O* equidistant from the source of illumination *L*. This rack pulls out from the side of the box and facilitates the rapid change of samples with minimum temperature drop in the thermostat. The magnesia block mounting is cut away under the tubes, so that the fading time may be checked by viewing the sample from above through W_2, as well as by direct transmitted light through W_1. The blower heater unit *B* was adapted from a 400-watt hair drier by soldering a circulating flue over the intake port, and by insertion of resistances and relay in the heater circuit. Since it was desired at various times to operate over a temperature range from 40° to 90° C., the most convenient resistance mounting was found to be lamp sockets, S_1, S_2, and S_3, mounted on the side of the box (S_1 and S_2 in parallel, with S_1 in series with relay and S_3 in series with fan motor, best values for operation at 70° C. were S_1, 50 watts, S_2, 100 watts, and S_3, 25 watts). When operating at other temperatures, or to maintain temperature at start of test before the irradiating lamp *L* is cut on, the necessary changes in resistance may be made easily.

Method. Clean, dry A. O. C. S. oil color tubes, graduated at the 25-ml. level, are filled to the mark with the oil or melted fat to be tested. One milliliter of a freshly prepared 0.025 per cent solution of methylene blue in anhydrous alcohol is added, and quickly mixed with the oil by shaking. The tubes containing the mixture are then brought to 70° C. by holding for a few moments in a steam bath, and the time is recorded when the samples are placed in the irradiation chamber. The end point is observed through the windows W_1 and W_2 and with most vegetable oils and hydrogenated fats the color change is quite abrupt at the end of the reduction period. The fading time is recorded in minutes, and unless otherwise indicated in the following data, the determinations have been made at 70° C., 0.001 per cent dye concentration, with 100-watt inside-frosted daylight Mazda lamp at 15 cm. from the center of the sample.

A few precautions are necessary to obtain consistent and reproducible results. Moisture must be excluded in all operations, and if the original sample contains more than traces of water it should be dried, care being taken to minimize oxidation in this operation. The methylene blue reagent should be prepared from aldehyde-free anhydrous alcohol, and can be kept satisfactorily for a few days in a stoppered bottle placed in a desiccator. A number of determinations have been made using aldehyde-free anhydrous propanol, but it has no apparent advantage over the lower alcohol. Newton (*9*) has emphasized the importance of thoroughly cleaning glassware which has been in contact with rancid fat, in connection with the incubation accelerated rancidity test, and it is likewise imperative to clean the color tubes carefully in the present method. It has been found that rinsing with a fat solvent, followed by a 30-minute boil in 20 per cent sodium hydroxide and overnight soaking in cleaning solution, serves the purpose very well. With most fat samples, the degree of accuracy of the method is determined by the personal factor in reading the end point. Colored oils rich in yellows and reds naturally give a green color with the reagent, and as the blue fades the green shades rather gradually to the original tint. However, visual observation of the end point has been found to be more satisfactory and reliable than the photoelectric method, for in spite of the use of color filters in connection with the latter, many natural oils and all-hydrogenated fats which have been examined give secondary color changes that interfere with photoelectric control. Since the methylene blue reduction period for most refined edible fats and oils does not exceed one hour, and the average is less than 30 minutes, it is not particularly tedious or inconvenient to record the end points visually.

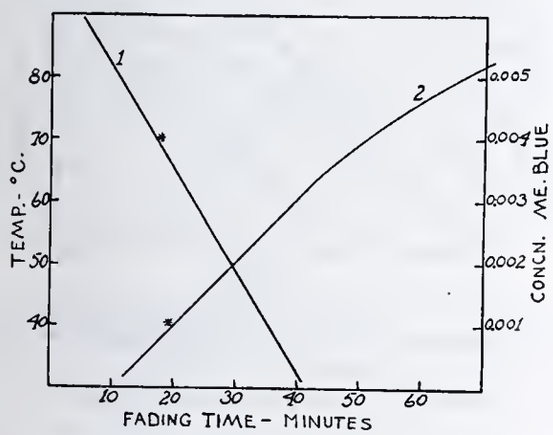

FIGURE 2. EFFECT OF TEMPERATURE AND METHYLENE BLUE CONCENTRATION ON FADING TIME

Tests made on freshly deodorized choice cottonseed oil.
1. Temperature–fading time curve
2. Concentration–fading time curve
* 70° C. and 0.001 per cent methylene blue concentration adopted as standard for control work.

The duration of the methylene blue fading time may be varied within certain limits by changing the reaction temperature, dye concentration, and light intensity. Figure 2 gives the values for freshly refined and deodorized cottonseed oil under the maximum range of conditions which have been found practical with the present apparatus. For control work on the estimation of stability of salad oils and shortenings, 70° C. and 0.001 per cent methylene blue concentration were adopted as standard conditions.

Figure 3 shows the comparative stabilities of four types of hardened cottonseed oil shortenings, aged in friction top cans at 90° to 95° F. Organoleptic manifestation of rancidity is indicated at the points designated by *R* on the methylene blue fading-time curves. All-hydrogenated shortenings are generally conceded to have superior keeping quality in comparison with compound types, and the fading-time curve 1 illustrates this point very well; 2 and 3 are two different grades of hydrogenated vegetable compound shortening, and having similar composition, the stability curves follow the same general trend. Curve 4 may be interpreted to show that the original sample was very close to a state of incipient rancidity, since the slope of the curve corresponding to the initial stage of the aging period resembles that of the other fats at a later stage in the test. While this inferior keeping quality of the oleo compound cannot be attributed entirely to the oleostearin content, it has generally been found that strictly vegetable compounds show a higher initial fading time. If, however, the curves are to be interpreted for practical purposes, it should be pointed out that the smaller slope and higher fading time during the later stages of the test on the oleo compound indicate that, although the original conditions of such fats may not be very good, the rate of change under ordinary storage conditions is slightly slower than the rate for vegetable compound.

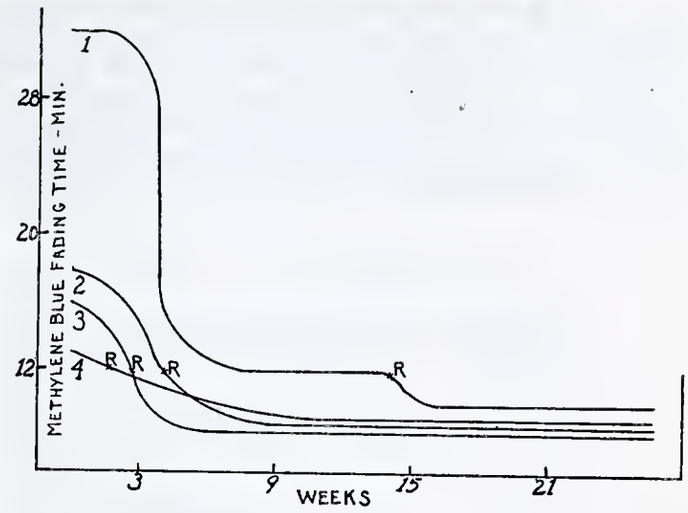

FIGURE 3. VARIATION OF FADING TIME (REDUCTION PERIOD) WITH AGE FOR DIFFERENT TYPES OF HYDROGENATED SHORTENING

1. All-hydrogenated
2. Package vegetable compound
3. Bulk vegetable compound
4. Bulk oleo compound

Certain metals in oil-soluble form are known to have a marked effect on the stability of fats, and Figure 4 gives the fading time of methylene blue in cottonseed oil to which very low percentages of some of the common metals have been added. Copper is a powerful pro-oxidant for autoxidation reactions (*1*) and the accompanying curve shows that only 20 p. p. m. reduce the fading time from 24 to 8 minutes. Manganese in somewhat higher concentrations likewise has a strong pro-oxidant effect, but ferrous iron,[1] divalent tin, and nickel at the low concentrations plotted on the graph have no effect on the fading time. Zinc apparently has a stabilizing action, but this point has not been checked by aging tests, and it is probable that the prolonged fading time in this case is due to some interaction of the zinc with methylene blue. Further work is being conducted on the applicability of the methylene blue reduction method in the presence of pro-oxidants and antioxidants.

Figure 5 presents keeping quality curves for a number of freshly refined and deodorized vegetable oils. Coconut oil

[1] Under oxidizing conditions, low concentrations of iron may shorten the induction period of fats and oils considerably. In one experiment, 0.00025 per cent of ferric stearate was dissolved in cottonseed oil, and the sample was aged by aëration and irradiation at 100° C. The rate of peroxide formation was accelerated greatly. In the present experiment, it is thought that oxidation of Fe^{++} to Fe^{+++} does not occur in the limited test period (24 min.). Generally speaking, the methylene blue test is not always reliable when applied to fats containing substances having a high reduction or oxidation potential.

has a high original fading time, but this falls rapidly to a value only slightly higher than that for corn oil after aging 5 weeks in glass at room temperature. Soybean oil gives an aging curve similar to corn oil, while the remaining oils are grouped quite closely. Peanut oil, at least this particular sample, proved to be the most unstable of the group. Since the histories of these oils prior to refining and deodorizing are

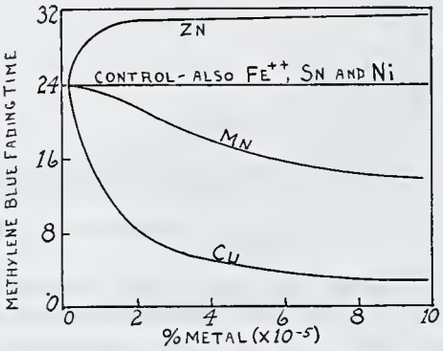

FIGURE 4. EFFECT OF METALS ON FADING TIME IN COTTONSEED OIL

Metals added as freshly prepared soaps of fully hydrogenated cottonseed fatty acids

not known, it is not possible to generalize from the data given on the relative stabilities of these oils as a class. For example, some of the oils may have been prepared from old or damaged seed, and some may have been extracted with solvents, as against pressing for others. This graph is merely presented to show that methylene blue reduction affords a convenient method for following the progress of oxidative rancidity in various kinds of oils.

The relation of fading time to Kreis number and peroxide value is shown by Figure 6. A sample of cottonseed oil was aged rapidly by aërating at 100° C. under intense illumination, so that a rancid odor developed in 2 to 2.5 hours. Six hours under these conditions sufficed to complete a test, sending the peroxide value (millimoles of peroxide) to 250. (A comparison of accelerated aging tests, with and without photocatalysis, has been included in another paper.) It may be said

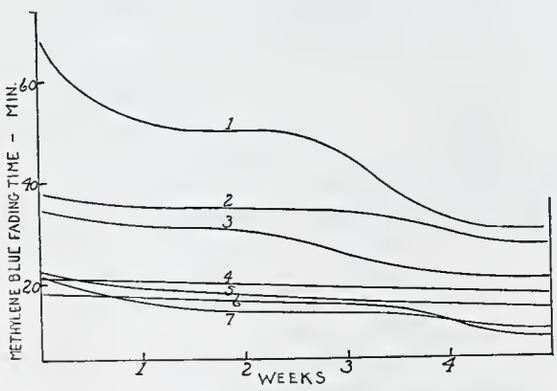

FIGURE 5. STABILITY CURVES FOR FRESHLY REFINED VEGETABLE OILS FROM DIFFERENT SOURCES

Samples aged at 90° to 95° F. in loosely stoppered glass bottles, exposed to diffused daylight.

1. Coconut
2. Corn
3. Soybean
4. Rape
5. Cottonseed
6. Peanut
7. Sunflower

here, however, that for pure cottonseed oil the shape of the aging curve is approximately the same in both cases, so that the light may be considered as a catalyst which does not markedly alter the type of reaction products which are operative in bringing about the color change in methylene blue. By the use of a 200-watt lamp at 15 cm. from the oil, employing a modification of Wheeler's (*13*) accelerated aging apparatus, the aging period has been reduced 100 per cent and more.

The peroxide value curve in Figure 6 shows the extent of the oxidative induction period, while the fading time and Kreis numbers follow a fairly constant inverse proportion. This may be interpreted to indicate that the oxidative decomposition products causing the Kreis reaction are responsible for the methylene blue reduction, whereas the concentration of peroxide as measured by Wheeler's method is better adapted to register the termination of the induction period, when fat samples are aged by aërating at high temperature. Like the Kreis test, the methylene blue method is most satisfactory when used on fresh nonrancid fats, or fats in a condition of incipient rancidity, in which a rancid flavor has not become pronounced.

Interpretation of methylene blue fading time for practical application to problems of processing and storage of fats and oils may best be indicated by referring again to Figure 3. All the vegetable shortenings used in this series were freshly bleached and deodorized at the beginning of the test. Thus, knowing the history of the fats, the initial fading times would

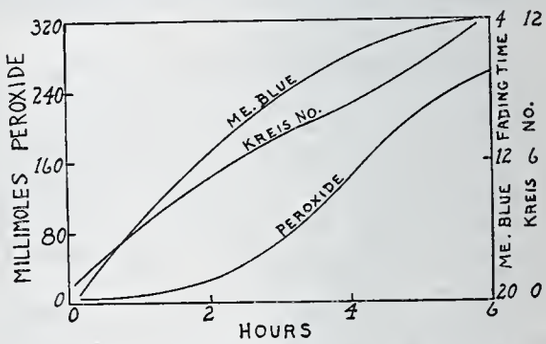

FIGURE 6. COMPARATIVE STABILITY CURVES ON COTTONSEED OIL SUBJECTED TO ACCELERATED OXIDATION AT 100° C.

Irradiated by 200-watt lamp at 15 cm. distance

be sufficient to classify the vegetable shortenings according to stability, in the order 1-2-3, with 1 standing considerably superior to 2 and 3. The oleostearin used in making the oleo compound had not been freshly deodorized, so that, although the initial fading time is the lowest of all, it would not be safe to conclude that this type of compound has the lowest stability. Subsequent values on the aging curve tend to show that if the oleo compound had had the same treatment as the other samples, the initial fading time would have been equal to or higher than 2 and 3. For the estimation of stability when testing samples of known history, the methylene blue method ranks with direct oxygen absorption (*13*), with the added advantage of a much shorter test period and simplicity of apparatus. Additional practical information on fat stability may also be obtained by using the methylene blue test in conjunction with accelerated aging, or low-temperature aging, when time is not the dominant factor. Wheeler's accelerated oxidation apparatus in a modified form is being used at present in this laboratory, and the reaction is followed by measuring the change in methylene blue fading time as well as increase in peroxide values.

ACKNOWLEDGMENT

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Determination of Formic, Acetic, and Propionic Acids in a Mixture

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PREVIOUS publications (*6*, *10–13*) have reviewed the literature and discussed the need for rapid and accurate methods for the quantitative determination of the volatile fatty acids in fermenting liquors. In these papers the application of the partition method to two acid mixtures was shown, together with theoretical discussions of the possibilities of the partition method in general.

The method presented in this paper is intended to deal specifically with the problems presented under the special conditions involved in the fermentative production of propionic acid. In the procedure described, the partition method is combined with a modified mercuric oxide oxidation for the separate determination of formic acid.

PREPARATION OF FERMENTATION LIQUORS

To prepare a fermentation liquor for the quantitative determination of the volatile acids, a quantity containing about 60 cc. of 1 *N* volatile acid is placed in a distilling flask, made neutral to phenolphthalein, and distilled until the residue in the flask reaches a volume of about 150 cc. The residue is then made just acid to Congo red paper with 1 to 1 sulfuric acid, boiled under a reflux condenser to remove carbon dioxide, and subjected to steam distillation. A constant volume of liquid in the distilling flask should be maintained. Two liters of distillate should be collected.

From Dyer's work (*2*) it is evident that under these conditions about 95 per cent of the formic and substantially all of the acetic and propionic acids will be removed from the fermentation liquors. Prolonged steam distillation should be avoided, because under these circumstances volatile acid may be produced from unfermented carbohydrate. Lactic acid also distills over to an appreciable extent, and for this reason the fermentation liquor should not be saturated with salt before steam distilling. Under the conditions imposed by Olmsted, Whitaker, and Duden (*5*) lactic acid in 600 cc. of distillate has been found equivalent to 22 per cent of that present in the original liquor.

Under the conditions of ordinary steam distillation some substances, such as lactic acid, distill over and may interfere with the analysis. A much more accurate analysis can be obtained if the first steam distillate is neutralized, evaporated to 150 cc., made just acid to Congo red, and redistilled according to Olmsted (*5*). Under these conditions the volatile acids will all come over in 1 liter of distillate. This distillate is then adjusted by dilution to an acid concentration of approximately 0.03 *N*, and this 0.03 *N* acid solution is used for the determination of the volatile acids.

DETERMINATION OF FORMIC ACID

Results obtained in this laboratory show that strong oxidizing agents, such as chromic acid or permanganate, cannot be used for the oxidation of formic acid in the presence of propionic acid, since some of the propionic acid is oxidized to acetic acid.

For example, a solution of 25 cc. of 0.1 *N* formic acid, 25 cc. of 0.1 *N* acetic acid, and 50 cc. of 0.1 *N* propionic acid was oxidized with a dilute permanganate solution for 30 minutes at boiling temperature. The formic acid was completely oxidized by this treatment. (The solution should remain acid, since propionic acid is oxidized to oxalic acid in alkaline solution, *4*.) After acidifying and distilling the residual solution subsequent to oxidation, the distillate should have contained 25 cc. of 0.1 *N* acetic acid and 50 cc. of 0.1 *N* propionic acid. Analysis showed, however, 52.5 cc. of 0.1 *N* acetic and 22.5 cc. of 0.1 *N* propionic acids—that is, about half of the propionic acid had been converted to acetic acid.

The use of dichromate (*9*) for the oxidation of formic acid in the presence of propionic is to be avoided for the same reason.

The most convenient method of determining formic acid is the mercuric chloride method of Auerbach and Zeglin (*1*), but serious errors are likely to be encountered by its indiscriminate use with such complex mixtures as fermentation liquors. It has been found by Weihe and by Wood in this laboratory, working independently with widely different substances, that the mercuric chloride method gives considerably higher results than are obtained by oxidation of the formic acid with mercuric oxide (unpublished data). These high results are apparently due to substances other than formic acid which reduce mercuric chloride, such as acetylmethylcarbinol. In consequence, it seemed advisable to use mercuric oxide for the oxidation of formic acid and to determine the formic acid by the carbon dioxide evolved, inasmuch as it is highly improbable that carbon dioxide would be evolved by action of mercuric oxide from substances other than formic acid.

If circumstances permit, any convenient method of determining formic acid, other than those involving oxidation with strong oxidizing agents, may be substituted.

PROCEDURE FOR DETERMINATION OF FORMIC ACID

The formic acid is oxidized with mercuric oxide. The carbon dioxide is absorbed in Bowen potash bulbs and weighed (*7*), or, if a mixture is being analyzed from which volatile substances may be carried over into the potash

bulbs, the carbon dioxide is absorbed in a Truog tower (*8*) and determined volumetrically.

Two hundred and fifty cubic centimeters of the acid solution, prepared for analysis as described above, are placed in a 500-cc. balloon flask and 5 grams of mercuric oxide added. The flask is connected through a reflux condenser to a Bowen potash bulb, or, if the volumetric method is used, to a Truog tower as described by Heck (*3*). A current of carbon dioxide–free air is started through the apparatus and the acid mercuric oxide mixture in the oxidation flask is gently boiled for 20 minutes. Twenty cubic centimeters of 50 per cent phosphoric acid are then added to the reaction flask and boiling and aëration are continued for 15 minutes. If the volumetric method is used the alkali is carefully washed down from the absorption tower into the flask (*3*), an excess of barium chloride is added, and the excess of alkali is titrated with 0.5 N hydrochloric acid, according to the procedure of Heck (*3*). Phenolphthalein is used as an indicator.

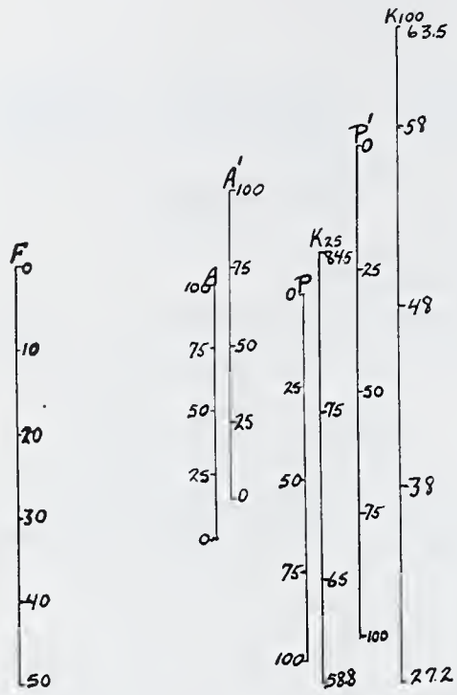

Figure 1. Nomogram for Determination of Acids

Under these conditions the formic acid has been found to be completely oxidized, while the other acids present remain unaltered.

Table I. Determination of Formic Acid in the Presence of Other Substances

Acids Present						CO_2 Calculated	CO_2 Found	Recovery of Formic Acid
Formic	Acetic	Propionic	Butyric	Lactic	Pyruvic			
%	%	%	%	%	%			%
100	0	0	0	0	0	0.0431	0.0436	101.1
100	0	0	0	0	0	0.0431	0.0440	102.0
100	0	0	0	0	0	0.0431	0.0423	98.3
100	0	0	0	0	0	0.0431	0.0430	99.7
25	25	50	0	0	0	0.0440	0.0444	101.0
20	20	40	0	20	0	0.0440	0.0442	100.5
11.1	11.1	22.2	55.5	0	0	0.0440	0.0437	99.4
50	0	0	0	50	0	0.0440	0.0447	101.5
50	0	0	0	0	50	0.0440	0.0432	198.3
0	50	50	0	0	0	0.0	0.0010	...
0	0	50	50	0	0	0.0	0.0015	...
...	..	..	..	..	..	0.0	0.0010	...

Representative analyses are shown in Table I. Formic acid is determined in the presence of various other acids as indicated, using the gravimetric method.

Determination of Mixtures of Acids

In many studies on the production of propionic acid by microörganisms, the mixtures of acids will contain acetic and propionic, with varying amounts of formic acid. Lactic acid may also be present. If mixed cultures of organisms are being used, fatty acids other than formic, acetic, and propionic may also be present.

The present method is designed to determine formic, acetic, and propionic acids quantitatively, when no other acids are present. A provisional method for the detection, but not for the identification, of foreign acids is included. The procedure is based on the determination of formic acid in an aliquot as given above. Another aliquot of the acid mixture is then partitioned between ethyl ether and water. By means of the data obtained, it is possible either to calculate the percentages of the other acids or to read them from the nomogram given in Figure 1.

Partition Method. The partition constants used in this procedure are obtained as follows:

A 300-cc. portion of the approximately 0.03 N acid solution, prepared as described above, is brought to a temperature of 25° C. Fifty cubic centimeters of the solution are titrated with 0.05 N alkali in the presence of phenolphthalein. Let M_1 represent the number of cubic centimeters of 0.05 N alkali required. Another portion of 55 cc. of the acid solution and 25 cc. of pure ethyl ether is pipetted into a 225-cc. separatory funnel and the mixture is shaken vigorously for 1.5 minutes. The temperature should be maintained at 25° C. After allowing 3 or 4 minutes for the phases to separate, 50 cc. of the aqueous phase are withdrawn into a 50-cc. volumetric flask and titrated with 0.05 N alkali. Let M_2 represent the number of cubic centimeters of alkali required. The partition constant is obtained from the equation $K = M_2/M_1 \times 100$. It is evident that this constant is actually the percentage of the acid which remains in the aqueous phase. This constant is not to be confused with the partition coefficient used in physical chemistry.

Constants for each acid were established in this manner. Solutions of the pure acids were made up to approximately 0.03 N and 55 cc. of each solution partitioned with 25 cc. of ether as described. The constants found are: formic acid, 84.5; acetic acid, 82.1; and propionic acid, 58.8.

If these three acids are present in a mixture in which the normality lies between 0.02 N and 0.04 N, the partition constant obtained for that mixture will be the sum of the partial constants of each acid.

For example, assume a mixture consisting of 10 per cent of formic acid, 30 per cent of acetic acid, and 60 per cent of propionic acid. The value of K, if accurately determined, would be

$$(84.5 \times 0.10) + (82.1 \times 0.30) + (58.8 \times 0.60) = K_{25} = 68.36$$

or the equation may be written

$$(0.845 \times 10) + (0.821 \times 30) + (0.582 \times 60) = K_{25} = 68.36$$

It must be noted that by the percentage of each acid is meant normality percentage, not percentage by weight. For example, the solution just mentioned would contain 10 cc. of 0.03 N formic acid, 30 cc. of 0.03 N acetic acid. and 60 cc. of 0.03 N propionic acid per 100 cc. of acid mixture. Normality percentage is used throughout this discussion. The percentage of each acid present will be designated as F, A, and P for formic, acetic, and propionic acid, respectively. For solutions containing only these three acids, F, A, and P must add up to 100.

With these conventions, the general equations can be written:

$$\begin{aligned} 0.845F + 0.821A + 0.588P &= K \\ F + A + P &= 100 \end{aligned}$$

Since F is determined separately, it is not one of the unknown values, and the equations may be written:

$$\begin{aligned} 0.821A + 0.588P &= K - 0.845F \\ A + P &= 100 - F \end{aligned}$$

Solving A and P in terms of K and F we have:

$$A = 4.291K - 1.103F - 252.36 \quad (1)$$
$$P = 352.36 + 0.103F - 4.291K \quad (2)$$

Once K and F are determined, the percentages of acetic and propionic acids are obtained by substitution in Equations 1 and 2, respectively.

Determination of Formic, Acetic, and Propionic Acids in a Mixture

Formic acid in 250 cc. of the steam distillate is determined as described above. If the volume of distillate is limited and if the procedure is thought advisable, the formic acid may be determined by means of mercuric chloride according to the method described by Auerbach and Zeglin (*1*). This determination may be made on a smaller volume of the solution. The factor for converting mercuric chloride to formic acid is 0.09745. The formic acid is expressed in terms of normality percentage as indicated above.

Fifty cubic centimeters of the acid solution are titrated very carefully with 0.05 N sodium hydroxide and phenolphthalein as indicator. Fifty-five cubic centimeters of the solution are then placed in a separatory funnel and shaken with 25 cc. of ethyl ether as described. After the two phases have separated, 50 cc. of the aqueous phase are titrated and the value of K is calculated. Example: 50 cc. of the original solution required 30 cc. of 0.05 N alkali. After partition, 50 cc. of the aqueous phase required 19.5 cc. of the alkali.

$$K = \frac{19.5}{30} \times 100 = 65.0$$

After F and K are known, A and P are calculated by substitution in Equations 1 and 2 given above, or read directly from the nomogram.

In laboratories where a large number of determinations are to be made, it is convenient to read the values of A and P from a nomogram, such as that shown in Figure 1.

Assume a solution of such composition that $F = 10$ and $K = 75$. Lay a straight edge on the chart so that it passes through 10 on the F line and through 75 on the line K_{25}. A and P are read directly on the lines labeled A and P. For the mixture assumed $A = 58.2$ and $B = 31.8$.

Representative analyses of mixtures of acids are given in Table II.

Table II. Determination of Formic, Acetic, and Propionic Acids in Mixtures

Acids Taken			Acids Found			
Formic	Acetic	Propionic	Formic	Acetic	Propionic	K_{25}
%	%	%	%	%	%	
20	40	40	20	40.7	39.5	73.44
40	40	20	40.4	39.6	20.0	78.35
10	35	55	9.7	35.3	55.0	69.59
5	80	15	5.9	78.8	15.2	78.71
0	30	70	0.0	30.0	70.0	65.75
0	70	30	0.0	69.9	30.1	75.10

Detection of Other Acids in Mixture

For this purpose, another set of constants was established as before, except that 60 cc. of acid were partitioned with 100 cc. of ethyl ether. Fifty cubic centimeters of the aqueous phase were removed and titrated as before. These partition constants for the individual acids, which will be designated as K_{100}, are: $F = 63.5$, $A = 58.5$, and $P = 27.2$.

In addition to these constants, the values of lactic, butyric, and valeric acids were also determined for K_{100} and for K_{25}. For lactic acid, $K_{100} = 84.5$; for butyric acid, 10.3; and for valeric acid, 7.9. The K_{25} values for these acids are: lactic, 90.0; butyric, 31.1; and valeric, 17.0. The value of K_{100} for the mixture of acids can be calculated in the same manner as for K_{25}.

$$0.635 + 0.585\,A + 0.272\,P = K_{100} \qquad (3)$$

This equation can be used for the detection of foreign acids in the following manner:

K_{25} and F are determined, and A and P calculated or read from the chart. Using these values from F, A, and P, K_{100} is calculated from Equation 3. K_{100} is then determined experimentally. If the calculated and experimental values of K_{100} agree, then no acids except formic, acetic, and propionic are present. If, however, the experimental and calculated values of K_{100} do not agree (within 0.4 unit), then other acids are present.

Table III shows the effect which the presence of other acids has on the value of K_{100}, as well as the errors which will occur in the determination of formic, acetic, and propionic acids when other acids are present. It can be seen that either lactic acid, butyric acid, or valeric acid will displace the determined value of K_{100} in the same direction.

Table III. Detection of Acids Other than Formic, Acetic, and Propionic

Acids Present										
Formic taken	Found	Acetic taken	Found	Propionic taken	Found	Foreign Acid	K_{25}	K_{100} Determined	K_{100} Calculated	Difference
%						%				
20	20	40	40.7	40	39.5	None	73.44	47.00	47.15	−0.15
40	40	40	39.6	20	20.0	None	78.35	54.24	54.25	−0.01
10	10	35	35.3	55	55.0	None	69.59	41.93	41.75	+0.18
5	5	80	79.8	15	15.2	None	78.71	53.88	54.00	−0.12
20	20	35	28	40	52	Butyric 5	70.51	44.77	43.2	+1.57
15	15	38	53.3	38	32.7	Lactic 9	74.82	50.23	48.9	+1.33
15	15	30	21.2	50	63.8	Valeric 5	67.64	41.12	39.3	+1.82
10	10	60	67.7	25	22.3	Lactic 5	77.15	52.71	52.00	+0.71
10	10	60	55.4	25	34.6	Butyric 5	74.34	48.95	48.20	+0.75
10	10	30	31	50	59	Lactic 5	68.64	42.20	40.50	+1.70
..	..	..	..	..	..	Butyric 5	...	...	...	....

In using the nomogram for the detection of foreign acids, A and P are read on the A and P lines as usual for F and K_{25}. The straight edge is now placed on F and on the same values of A and P except that the values are now located on the A' and P' lines. K_{100} is now read at the intersection of the straight edge with K_{100} line. This value of K_{100} corresponds to the calculated value of K_{100} as given just above. If no foreign acids are present, this value as read on the K_{100} line will be the same as the value of K_{100} determined experimentally.

An example will make the meaning clear. In the fifth mixture given in Table III, $F = 20$ and $K_{25} = 70.51$. As read from the chart, $A = 28.0$ and $P = 52.0$. The straight edge is then placed across $F = 20$ on the F line, $A = 28$ on the A' line, and $P = 52$ on the P' line. The value of K_{100} as read on the K_{100} line is 44.77.

Since lactic acid with a constant of 84.5 and valeric acid with a constant of 7.9 bring about a deviation of the constants in the same direction, it is manifestly impossible to have any combination of acids present as impurities which would escape detection by balancing each other in their individual effect on the final constant. The only foreign acid which might escape detection, if present in an amount over 5 per cent, would be an acid with both constants (K_{25} and K_{100}) very close to those of one of the three acids included in the quantitative method.

If desired, A and P could be calculated in terms of F and K_{25}. The acids could be determined by using both constants. If the values for A and P came out the same in each case, only the three acids would be present. If the percentages of A and P came out different, some other acids would be present.

Construction of Nomogram

The construction of the nomogram offers no great difficulty.

On a common base line the perpendiculars F and K_{25} are erected at any convenient distance apart [10 inches (25 cm.) serves very well]. F is 25 cm. in length, and K_{25} has a length in centimeters corresponding to the difference between the constants for formic and propionic acids: 84.5 − 58.8 = 25.7 cm. K_{25} is calibrated in centimeters from $K_{25} = 58.8$ to 84.5 as shown. F is calibrated from 0 to 50 in the opposite direction. A line is drawn from $K_{25} = 84.5$ to meet F extended to $F = 100$. F may actually be extended, or the point of intersection of the diagonal with the base line may be calculated geometrically. Another diagonal is drawn from $F = 0$ to $K_{25} = 58.8$. The two diagonals intersect at the point $A = 0$. The line A is

drawn parallel to F and K_{25} from the point $A = 0$ to the point of intersection of the line from $F = 0$ to $K_{25} = 82.1$ (the K_{25} value for pure acetic acid). This A line is calibrated upward from 0 to 100. The point $P = 0$ is located at the point of intersection of the lines, $F = 0$ to $K_{25} = 82.1$, and $K_{25} = 84.5$ to $F = 100$. The line P is drawn parallel to K_{25} to intersect the diagonal, $F = 0$ to $K_{25} = 58.8$. The line is calibrated downward from 0 to 100.

The A', P', and K_{100} lines are located in the same manner. Some convenient unit of division is selected for the K_{100} line. The length of line is then measured off from $K_{100} = 27.2$ to $63.5 = 27.34$ units. The line is then located so that the upper end just meets the diagonal extended through $P = 0$ and $K_{25} = 84.5$. The extremities of the A' and P' lines are then located in the same manner as those of A and P.

Discussion

The method of analysis given is based on an approximately 0.03 N acid solution as a matter of convenience. At least 2000 cc. of steam distillate must be collected in order to drive all of the volatile acids over. Usually such a quantity of liquor can be used as to give 2 liters of 0.03 N acid distillate, and the analyses can be made without further treatment of the distillate.

Table IV. Determination of Organic Acids at Different Concentrations

Normality	Acids Taken			Acids Found		
	Formic	Acetic	Propionic	Formic[a]	Acetic	Proponic
	%	%	%	%	%	%
0.1[b]	25.0	25.0	50.0	25.0	24.0	51.0
0.06	33.3	33.3	33.3	33.3	32.0	35.0
0.06	33.3	33.3	33.3	33.3	33.3	33.3
0.02	33.3	33.3	33.3	33.3	34.5	32.2
0.015	33.3	20.0	66.6	33.3	21.3	65.2
0.015[c]	13.3	20.0	66.6	33.3	20.8	66.0
0.020	20.0	30.0	50.0	20.0	31.4	48.5
0.020	20.0	30.0	50.0	20.0	29.5	50.5
0.020	33.3	33.3	33.3	33.3	34.5	32.2

[a] Actual amount of formic acid present, no determination made.
[b] One-half volume each of ether and acid taken.
[c] Double volume each of ether and acid taken.

The effect of concentration of the acids on the determinations is shown in Table IV. Apparently the method holds reasonably well for the ranges of concentration given, but is recommended only for 0.03 N acid, especially for the provisional detection of contaminating acids. More accurate results could be obtained with 0.1 N acids if the method were adapted to that concentration, because larger titration figures could be used—for example, there would be less experimental error involved if figures such as 40/50 could be used instead of 4/5. The titrations must be done with extreme accuracy. In the hands of a careless worker, errors may easily arise which would indicate the presence of 5 or 10 per cent of some foreign acid. The pipets and burets should be carefully standardized. All water used should be free from carbon dioxide. The method is rapid and reasonably accurate if properly executed.

In using the qualitative scheme devised here, it is advisable to ignore differences in K_{100} of less than 0.4 units, which would indicate the presence of approximately 3 per cent of lactic or butyric acids, or 1 or 2 per cent of valeric acid. If the K_{100} values are appreciably different from each other, it would be well to check the determinations before spending much time trying to identify any contaminating acids which may be present. The scheme should be used with judgment. Unfortunately no clue will be given as to the nature of any contaminating acids which may be encountered. If significant quantities of such acids are indicated, it is advisable to take 500 cc. of the solution, distill off 250 cc., and make a new set of determinations on the residue. If the contaminating acids are more volatile than propionic acid, the two K_{100} values will be closer together than they were before, since the impurities distill out faster than do the three acids under consideration. If such an acid as lactic is the contaminant, the K_{100} values will be more divergent than they were before. The ultimate identification, of course, would involve the preparation of a derivative.

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Gas Bubbler for Very Small Pressure Drops

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It is frequently necessary to have a gas absorber which will operate with a small pressure drop in the gas stream and yet have a small gas volume in the system. Such is often the case where thermal conductivity cells are used for gas analysis. In such cases, in order to prevent time lag in the analysis it is essential to keep the volume of gas in the apparatus down to a minimum. This rules out the use of solid absorbent towers. If, in addition to the small gas volume requirement, it is necessary to have only a small pressure drop through the apparatus, it is frequently difficult to get efficient absorption of one of the gaseous constituents.

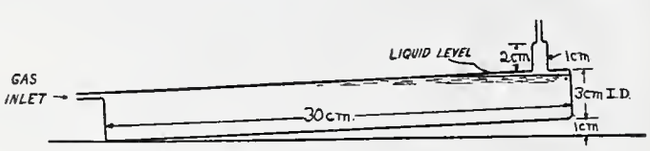

Figure 1. Inclined Absorption Tube

By using a large glass cylinder nearly filled with liquid, placed on a slight incline, it is possible to obtain sufficient contact between gas and liquid for efficient absorption and the static head to be overcome can be kept very small.

The apparatus shown in Figure 1 has been found very satisfactory when filled with potassium hydroxide for absorbing carbon dioxide from gases containing 1 to 90 per cent with a gas velocity up to 50 cc. per minute. It has also proved satisfactory when filled with concentrated sulfuric acid for absorbing water from gases saturated at 25° C.

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Microscopic Examination of Rubber and Other Solid Technical Products

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A method for preparing sections for microscopic examination is described. The method is of general application to raw materials and semi-finished or finished products of the rubber industry, and is of especial value for preparing sections of composite materials, whose constituents differ widely in hardness. The samples are hardened by curing and impregnation with molten sulfur and are then polished by variations of the usual metallographic methods and examined by reflected light. An application of the method to the quantitative estimation of the degree of dispersion of pigments in rubber stocks is outlined. Illustrations show some applications of the method of examination to a variety of products.

The preparation of materials used or made in a rubber factory for microscopic examination presents numerous difficulties. A part of the raw materials and nearly all of the semi-finished and finished goods are tough and elastic, opaque, and composite in structure. Rubber itself, cured or uncured, is very difficult to section and when combined with copper or iron wire, cotton, asbestos, or coarse mineral fillers, it is almost impossible to prepare. Allen (*1*) has reviewed previous work and detailed his own method. Steele (*12*), Pohle (*7*), and Grenquist (*6*) have made additional contributions. All these methods now in general use employ either extremely thin transparent sections that are of limited size or rough opaque sections that are unsuitable for even moderate magnification.

In a series of papers published in 1905 (*3*), Breuil suggested, among other methods for examining rubber, an adaptation of metallographic methods. Because of inferior equipment, his results were not very useful, and he abandoned this method in favor of transparent sections. The present paper is a description of a somewhat more successful attempt to apply metallographic methods to rubber fabrications.

The general methods for preparing, examining, and photographing opaque materials, as described by Chamot and Mason (*4*), have already been applied to a limited extent to technical products (*9, 10, 11*). The procedure developed by the author for rubber and similar materials is much the same, but requires a method for the preliminary hardening of the sample that will not disturb its structure. The most suitable hardening method has been found to be a cure in molten sulfur, which thoroughly impregnates any porous structures as well as hardens the rubber structure itself.

Preparation of Samples

The sample to be examined may be of any size necessary, but for convenience in manipulation, large surfaces should be cut into blocks no larger on the face to be polished than 2 cm. to the side. Hard rubber and hard asphaltic compositions usually need no further hardening treatment, but if they contain textile fibers, these can be more successfully polished if they are supported and made brittle by the molten sulfur cure. To avoid blowing, it is best to give uncured stocks a preliminary quick press cure such as that used for gravity samples. This preliminary press cure does not seem to affect the dispersion materially, but it will seriously disturb directional effects where these are of importance.

The samples to be hardened are cut with one suitable face roughly plane and are then immersed in a bath of molten sulfur at 135° C. for 12 to 24 hours. Excessive temperatures must be avoided to prevent blowing of the stock and distillation of volatile constituents. The cold sample, after a proper cure, will have a surface layer several millimeters thick, of a tough hornlike consistency too hard to be dented with the fingernail.

For the grinding and polishing of the hardened samples in the present work, an automatic polishing machine after the design of Epstein and Buckley (*5*) was used. Where such a machine is not available, entirely satisfactory results can be obtained on a simple variable-speed polishing lap, or by an adaptation of Pulsifer's hand-block methods (*8*).

The samples are first flattened on a coarse loose-bonded silicon carbide grinding wheel (Norton's 3760J5T-2) thoroughly flushed with water and operating at about 300 r. p. m. The very important rough polishing is accomplished on a wheel covered with wool broadcloth charged with a paste of "600" silicon carbide in water at 300 r. p. m. After a thorough rinsing to remove any trapped coarse material, the sample is given its final polish on a wheel covered with cotton-backed silk velvet charged with a small amount of a special magnesium oxide (Shamva) in water. The samples are finished off by flooding this last lap with quantities of water, which removes all the powder film and leaves the sample with a clean, bright, easily dried surface.

The finished samples can be examined and photographed in a manner identical with that used for metal specimens (*4*), using any good vertical illuminator and short-

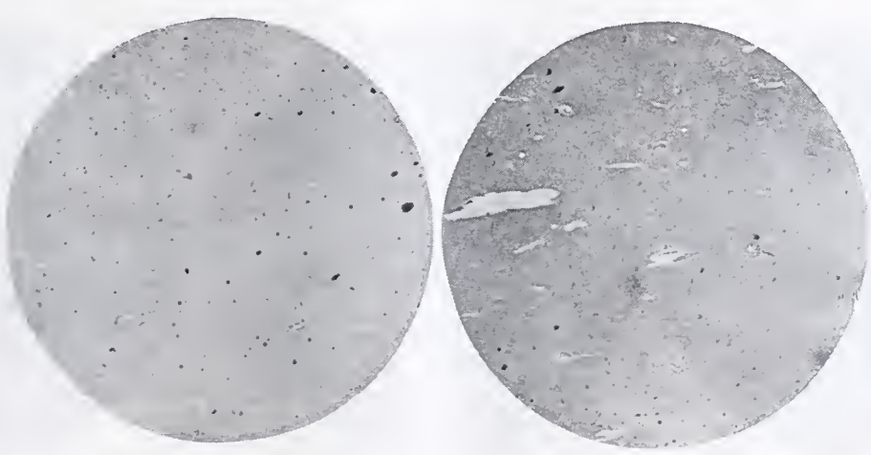

Figure 1. Tire Tread Stocks, Containing (1) Good-Dispersing and (2) Poor-Dispersing Gas Black (× 64)

Black spots are polishing pits in the surface

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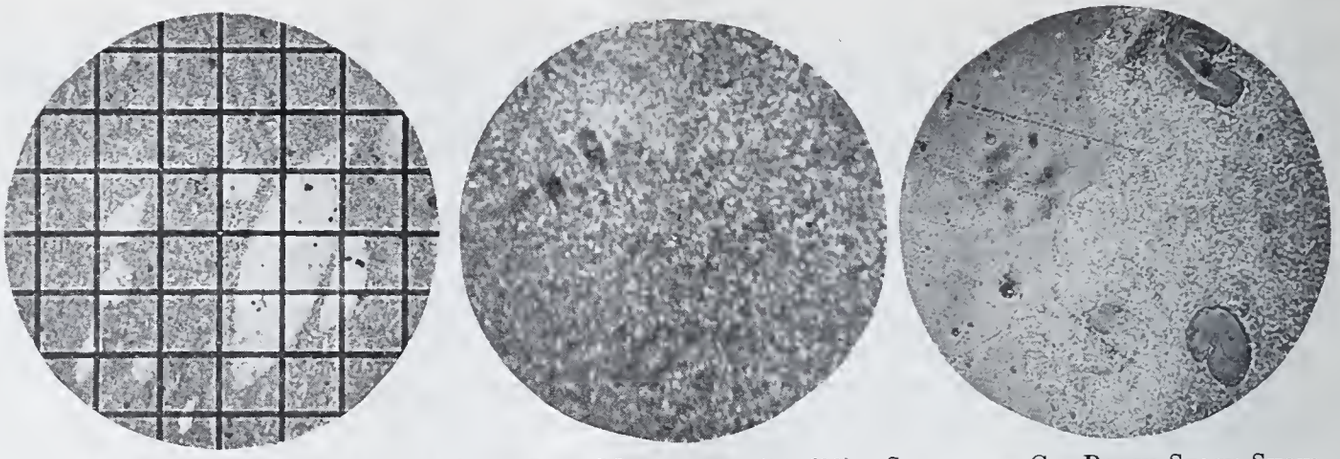

FIGURE 2. GAS-BLACK STOCK WITH CROSS-LINE MICROMETER (× 600). SURFACE OF GAS-BLACK STOCK SHOWING GRANULAR MATRIX (× 1350). BOUNDARY OF PURE GUM AND RECLAIM CARCASS STOCKS (× 600)

mount objectives. Well-corrected lenses and careful adjustment of the illumination are essential, because of the absence of color and the low contrast in the specimens. Magnifications up to 600 can easily be utilized and useful observations have been made at 2300, using well-corrected oil-immersion objectives. Auxiliary methods of illumination that have been found useful in interpreting structures are polarized reflected light, filtered colored light, and fluorescence from ultra-violet light.

APPLICATIONS

The most useful application of this method of examining rubber has been in the quantitative estimation of the degree of dispersion of pigments in rubber mixes, particularly tread stocks. The term "degree of dispersion," as used in the rubber industry, is rather indefinite in its connotation. For the purposes of the present work, it is taken to mean the degree of freedom from discontinuities visible to the unaided eye or by the use of a moderately powerful microscope. These discontinuities may be sand, grit, wood, free pigment, or unblended master batch. They are arbitrarily considered significant if they are readily measurable at 600 magnification, using "daylight" illumination and good optical equipment.

The samples prepared as previously described are examined under the conditions specified above, using a net-micrometer in the ocular. The area of individual particles of undispersed material is estimated in terms of the squares of the micrometer, and the per cent of the area of the field occupied by undispersed material is calculated. This procedure is repeated on a number of fields distributed over the surface of the section, and the average value is found. For well mixed treads, the average value based on a measurement of forty fields gives a value reproducible to a few per cent. For master batches and similar mixes, the average value of ten fields is of sufficient accuracy. Other methods of areal analysis might be used (*1*), but this has been found to be the most convenient. Alling and Valentine (*2*) have shown that when a sufficient number of plane sections of a solid are examined, the average areal percentage of any component is the same as the volume percentage of that constituent. This is the value designated as "per cent undispersed material by volume." This method of estimating dispersion has been used in studying milling operations, in judging the dispersibility of pigments, and in rating the value of dispersing agents.

This and other applications of the method are illustrated in the photomicrographs. Figure 1 shows the appearances of two tread stocks processed in the same way, but containing good-dispersing and poor-dispersing carbon blacks. The white areas are areas of poor dispersion. Figure 2 shows the surface of a gas-black stock as it appears in conjunction with the ocular net-micrometer for quantitative determinations of dispersion; the surface of a gas-black stock at very high magnification; and the boundary between two stocks of different composition. Flow and mixing at boundaries can be studied in this way.

Figure 3 shows the application of the method to composite structures. The first photomicrograph, at low magnification, shows the relative positions of the cords in a heavy tire carcass. The second is a portion of one of the same cords at high magnification, showing the appearance of the cross section of the individual fibers. The third shows the possibilities of the method when applied to composite materials, the constituents of which differ widely in hardness. This tire bead section contains soft rubber, semi-hard rubber, cotton, and steel wires.

FIGURE 3. COMPOSITE STRUCTURES

1. Cross section of tire carcass (× 8). 2. Cross section of tire cord showing individual cotton fibers (× 600). 3. Cross section of tire bead area (× 8)

Figure 4 is representative of the analytical possibilities of the method. It gives a photomicrograph of a fragment of wood, identified by its cellular structure, embedded in a tire tread. Following this lead it was found possible to prepare sections of wood by this method, as in the second photomicrograph.

Another highly complex subject is illustrated in Figure 5. Brake linings are complex fabrications of semi-hard rubber, asphaltic material, cotton, asbestos, and copper wire. The second photomicrograph shows the boundary between rubber and solid brass in a product depending on the adhesion of rubber to metal for its usefulness.

These photomicrographs suggest the possibilities to which this method for the microscopic examination of technical products may be put.

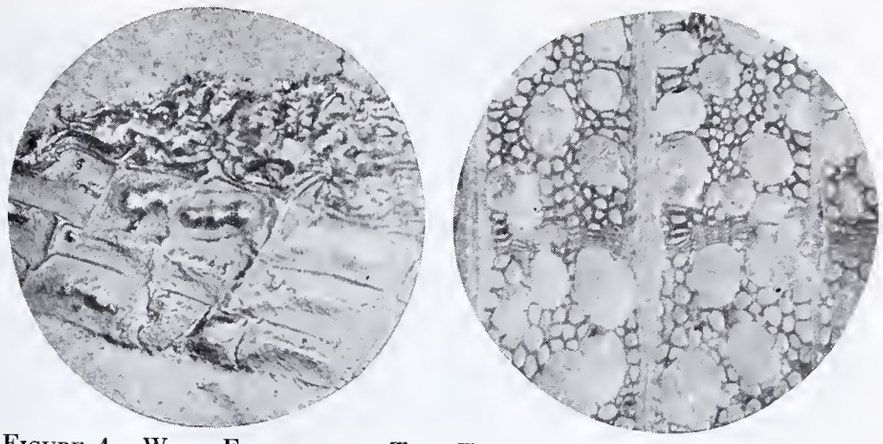

Figure 4. Wood Fragment in Tire Tread (× 600). Polished Section of Sycamore Wood (× 64)

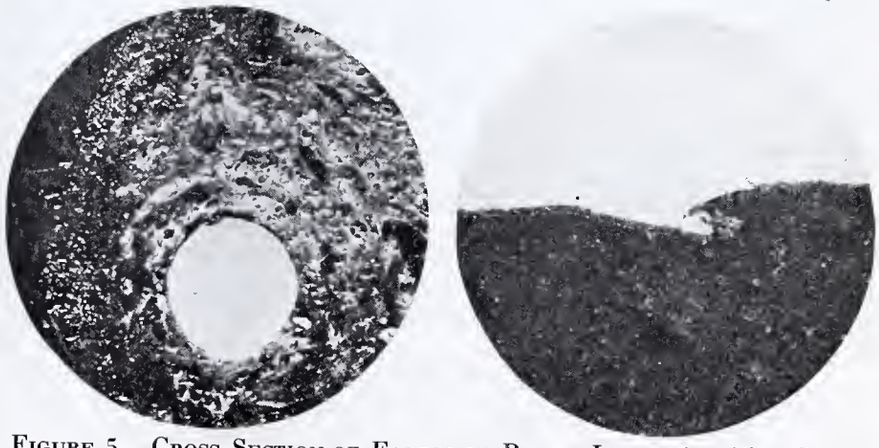

Figure 5. Cross Section of Fabric in Brake Lining (× 64). Cross Section of Adhesion Zone, Rubber to Solid Brass (× 600)

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Volumetric Potassium Bromate–Bromide Titration of Furfural

Effect of Temperature

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In 1923, Pervier and Gortner (*4*) published a method for the electrometric titration of furfural by potassium bromate. Youngburg and Purcher (*5*), Kline and Acree (*3*), and Iddles and Robbins (*2*) report difficulty in obtaining a good end point, or failure to check the method against other methods.

Using fresh solutions of furfural in ethyl alcohol, the author was unable to obtain theoretical titrations, the titer being several per cent too great. Investigation disclosed that at temperatures of about 18° C. theoretical values could be obtained, while at 27° C., the laboratory temperature, more bromine was used than expected. Gortner (*1*) stated that the investigations of Pervier and Gortner were conducted during the winter at 15° to 18° C. and that the temperature coefficient was not investigated.

Determinations of furfural made by the author by the electrometric method suggested by Gortner and Pervier gave an end point of 20.37 cc. at 10° C., 20.75 cc. at 20° C., 21.05 cc. at 24° C., and 21.80 cc. at 36° C., with the theoretical titer (0.09904 gram of furfural) of 20.62 cc., indicating that an increasingly greater titer is obtained as the temperature at which the reaction takes place is increased.

Kline and Acree (*3*) state that the end point is indefinite because of a second reaction involving the combination of another molecule of bromine with furfural. The extent of the secondary reaction is influenced by temperature, becoming especially marked at temperatures around 50° C.

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Simplified Method for Microdetermination of Iodine in Eggs

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THE iodine content of eggs has been a matter of much interest in recent years, because eggs with a high iodine content are a convenient source of iodine in the human dietary and may be of value in the cure or prevention of iodine deficiency diseases. Iodine may easily be incorporated in eggs by adding iodine compounds to poultry feeds.

The principal problem in the microdetermination of iodine in eggs is the removal of large quantities of organic material without an appreciable loss of iodine. Various methods given in the literature for the microdetermination of iodine in biological substances were found to be unsuitable or inconvenient in the analysis of eggs. The digestion with sulfuric acid and hydrogen peroxide, as described by Pfeiffer (*3*), is unsatisfactory because of incomplete oxidation, the distillation of fatty acids and other substances, and the inability to use large quantities of material. The fusion with potassium hydroxide and nitrate, as described by Kelly and Husband (*1*), requires such large quantities of reagents as to introduce considerable danger of contamination and difficulty in handling. Liquid eggs are not adaptable to combustion tube methods such as have been devised by McClendon (*2*), while a thorough drying of the eggs previous to combustion is undesirable.

Procedure

A procedure developed in this laboratory is simple and requires no costly or complicated apparatus.

The liquid contents of a number of eggs are placed in a flask, an equal volume of 95 per cent ethyl alcohol and 10 grams of c. p. potassium hydroxide per egg are added, and the mixture is boiled gently under a good reflux condenser for 16 to 24 hours. The boiling takes place without foaming or bumping. The product is a dark brown liquid containing very little solids. An amount of this liquid equivalent to 1 egg is placed in a 500-cc. nickel crucible and evaporated to dryness on a hot plate. Nickel crucibles are to be preferred, but may be replaced by Pyrex beakers. The crucible (or beaker) and contents are placed in a muffle furnace and ashed for about 4 hours at about 600° C.

The ash is extracted with 50 cc. of hot water, the extract filtered off, and the residue washed with hot water, the washings being run into the filtrate. The filtrate is acidified carefully with 6 *N* sulfuric acid to the acid point of methyl red. Five drops more of acid are then added. Saturated bromine water is added to the solution until it has a permanent, strong yellow color. The excess bromine is boiled off and the solution evaporated to about 15 cc. on a steam bath, cooled, and transferred to a small separatory funnel. Any crystalline material formed during cooling and evaporating is removed and washed. The washings are added to the solution.

A crystal of potassium iodide is added and the iodine formed is extracted with five 1-cc. portions of purified carbon tetrachloride in a small separatory funnel. The iodine in the carbon tetrachloride is determined colorimetrically by comparison with standard solutions of iodine in carbon tetrachloride. Corrections for the iodine content of the reagents used are determined by following the same procedure.

The colorimeter used is the Bausch and Lomb 3650-1 hydrogen-ion colorimeter. The capacity of the colorimeter cells is about 5 cc. Light is provided by a 75-watt frosted lamp in the Bausch and Lomb colorimeter lamp 2414. A blue glass filter is included in the eyepiece of the colorimeter.

The digestion of liquid eggs in alcoholic potash before ashing insures a more complete recovery of iodine. For example, a sample of mixed liquid eggs was found to contain 250 gammas (millionths of a gram) of iodine per egg by the alcoholic potash digestion method, while the ashing of the dried egg after an intimate mixture with a large excess of alkali gave an average value of 210 gammas, or only 84 per cent of the first value. The treatment with alcoholic potash probably converts the organically bound iodine into iodide ion and thus stabilizes it to the action of ashing.

The efficiency of the alcoholic potash digestion method in the recovery of iodine was tested by adding a number of inorganic and organic iodine compounds to liquid egg material of known iodine content and determining the total iodine in the mixtures. The results of these recovery experiments are given in Table I. By the alcoholic potash digestion method the iodine content of eggs has been determined over a range of 3 to 1750 gammas, with consistently good check results, during the routine analysis of eggs at this laboratory. This method may prove of value in the analysis of other biological materials.

Table I. Recovery by Alcoholic Potash Digestion Method of Iodine Added to Eggs

Iodine Compound Added		Iodine Content per Egg	Iodine Added per Egg	Iodine Determined per Egg	Iodine Recovered
		Gammas	*Gammas*	*Gammas*	%
Potassium iodide	a	12	50	61	98
	b	12	50	63	102
	c	12	50	61	98
Potassium iodate	a	12	50	62	100
	b	12	50	61	98
Iodosalicylic acid	a	12	50	62	100
	b	12	50	61	98
	c	12	50	62	100
Iodobenzoic acid	a	12	50	61	98
	b	12	50	62	100
Desiccated thyroid gland	a	12	50	63	102
	b	12	50	61	98
Potassium iodide	Av. 3 dets.	6	100	106	100
Iodosalicylic acid	Av. 3 dets.	6	30	36	100
Desiccated thyroid gland	Av. 3 dets.	3	40	41	95

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Correction

In the paper on "Use of the Slide Rule in Calculating Hydrogen-Ion Concentration and pH Values" [Ind. Eng. Chem., 5, 21 (1933)] the second sentence in the second example should read "0.477 is read on the *L* scale under 0.3339 on the *CI* scale."

M. C. Sanz, Jr.

Quantitative Isolation of Ether from Dilute Solutions

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In a previous paper (*1*) the authors described a method for the qualitative isolation of ethyl ether from very dilute solutions. The success of this procedure and the request for a quantitative isolation led the authors to modify the apparatus to permit quantitative or nearly quantitative collection of the isolated ether.

In the present paper no attempt is made to describe a highly sensitive or a perfectly quantitative method for the determination of ether. Other excellent procedures for this purpose already exist (*2–5*). However, in many cases, as for example in medico-legal work, it is highly desirable to recover and determine the ether as such, rather than a product of its decomposition. When isolated as such, the ether can be identified after measurement by further tests (odor, boiling point, vapor density, specific gravity, refractive index, solubility) and the possibility of error due to the presence of other substances such as acetone, which may interfere with the purely chemical determinations, is reduced or eliminated.

Apparatus

The experiments described below have been carried out with solutions of 10 to 400 mg. of ether in 50 to 100 cc. of water. The apparatus used (Figures 1 and 2) consisted of the rectification flask *A*, the receiver *B*, and the cooling tube *C*. The rectification flask *A* was essentially that employed in the qualitative experiments. It was necessary to modify it somewhat as the ether was to be collected in a separate vessel which, after centrifuging, would permit the immediate reading of the volume of the distillate. Part *h* of the rectification tube therefore had a bore of only 2 mm. and was bent downward as shown in the figure. The small bore of the outlet *h* made it necessary to provide an inlet tube *a* for filling and emptying the bulb. For filling, a small funnel is placed on the opening of the inlet tube. During the distillation a piece of glass tubing *d*, sealed at one end, is inserted into the rubber tubing *b*. Finally the bulb is emptied automatically by connecting with a siphon *c*, previously filled with water. This type of inlet may also be used to advantage in the qualitative apparatus.

The outlet tube *h* projects into the wide part *m* of the receiver *B*. The latter is a centrifuge tube calibrated to read directly in cubic millimeters or milligrams of ether. In order to permit the reading of small volumes with sufficient precision, the lowest part *o* of the tube had a bore of 2 mm. and part *n* had a bore of 4 mm. The capacity of the narrow part *o* (30 mm. height) was 150 cu. mm. and the capacity of part *n* (30 mm. height) was 350 cu. mm. The tube was calibrated with distilled water. As it was impractical to calibrate the conical portion of the tube between *o* and *n*, the expedient of dropping in a glass rod *p* to raise the level of the liquid to the calibrated portion of the wider tube *n* was employed. As the volume of the immersed rod was known, this could be subtracted from the volume given by the level of the liquid and the true volume of the latter readily ascertained. The special shape of the upper end of the receiver *B* was designed to prevent the dripping of the tube through the cork *k* and to decrease the loss of liquid by evaporation. Cork *k* fitted the metal tubes *E* of the centrifuge as well as the central bore of the cork *l*. The latter was slotted at the side to provide for the escape of the carbon dioxide and served for holding the receiver *B* in the proper position in the cooling tube *C*. The cooling tube was filled with crushed solid carbon dioxide and acetone. Care was taken that sufficient solid carbon dioxide was added so that some remained after the experiment was over. Otherwise a supersaturated solution of carbon dioxide is formed and from time to time the excess carbon dioxide is suddenly evolved and the acetone blown from the tube. It is advisable also to fill with solid carbon dioxide the crucible *D* which supports the cooling tube. A circular cardboard disk with a hole in the center to permit the receiver to project through was placed over the cooling tube to prevent the tiny droplets of acetone which are continually sprayed out of the cooling tube from reaching the interior of the receiver.

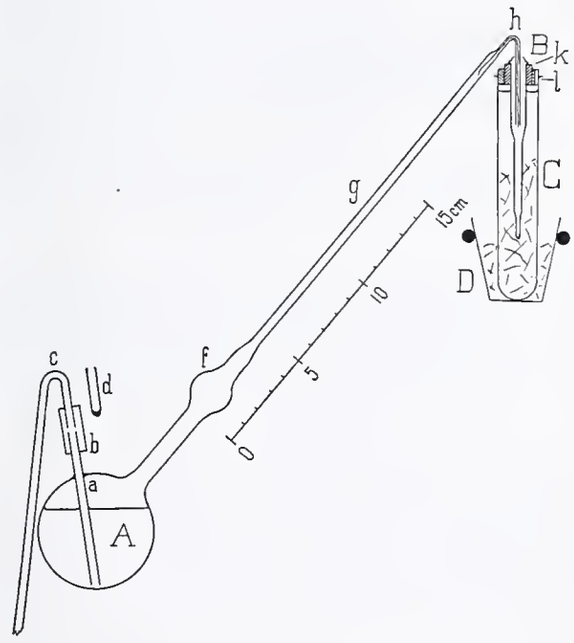

Figure 1. Diagram of Apparatus for Isolation of Ether by Distillation

In order to prevent condensation of the ether in the outlet tube *h* of the fractionating flask and still permit it to condense in the receiver, a copper wire (0.5 mm. diameter) was inserted in the outlet tube *h* as shown in the figure. (An electrically heated wire might be more efficient.) It was thought that if the end of the wire above the bend of the tube were heated by steam, the rest of the wire would become warm and vaporize the ether condensed in *h*. To accomplish this, however, it is necessary to hold the ring of steam condensate for about 1 to 2 minutes at the bend of the tube.

Procedure

Rectification flask and receiver were first carefully treated with cleaning solution and then rinsed out well. The rectification flask was then clamped into position and the portion from *f* upward dried by stroking with a Bunsen flame. The

[1] Now at Rutgers University.

receiver was dried by sucking through air by means of a capillary connected to a suction pump.

When the rectification tube had cooled to room temperature, a small portion of finely granulated zinc metal was introduced through *a*. Then 50 to 100 cc. of the ether solution were measured in a graduated cylinder, and poured into the bulb by means of a small funnel connected with *a*, and the inlet was promptly closed. Then the outlet *h* was inserted in the receiver, which was already immersed in the tube containing solid carbon dioxide and acetone. The solution in the bulb was heated to boiling with a microburner which permitted perfect regulation of the size of the flame and boiled until a ring of steam condensate appeared above *f*. At the same time all the ether had already collected above the ring of steam condensate as a layer of heavy vapor. The size of the microflame was then carefully regulated so as to cause a very slow ascent of the ring of steam condensate through *g* up to the highest point of the tube (bend). The ether vapor was driven up in front of the ring of steam condensate and, because of its high density, flowed down into the receiver as soon as it was driven beyond the bend into the descending part of tube *h*. Liquid ether was observed in the lower part of the tube *g* only with large quantities of ether. But condensation of the ether vapor always took place on contact with the cold copper wire. To evaporate also the ether in the lower part of *h* which was immersed in the receiver, the ring of condensate was kept at the bend for about a minute by proper regulation of the size of the micro flame.

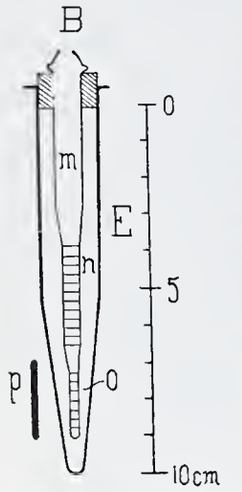

Figure 2. Calibrated Centrifuge Tube

The receiver was then lowered and removed without changing the rate of boiling (the ring of condensate always staying at the bend of the tube). Should the boiling be stopped before removing the receiver, the condensation of steam creates a partial vacuum in the rectification flask and the air rushing into it through the receiver draws considerable ether vapor with it, causing an appreciable error. In this case it is necessary to boil the solution up again and hold the ring of condensate again for a minute at the highest point.

Finally the receiver was taken out of the cooling tube and quickly transferred into the metal tube of a hand centrifuge (Figure 2) and the liquid contents were centrifuged (15 seconds) to the calibrated portion. The reading was taken after the tube had warmed to room temperature and the position of the meniscus no longer changed. Water vapor which came over with the ether froze out as ice on the upper walls of the receiver. When the centrifuging was done while the tube was still cold, this ice did not melt and therefore remained on the walls of the uncalibrated upper portion of the receiver. On warming to room temperature, the ice turned to small droplets which also remained adhering to the walls of the tube and did not interfere with the determination.

To prepare the apparatus for the next distillation, the solution in *A* was boiled for 5 minutes and the steam allowed to escape through *h*. The remaining liquid was removed from the bulb by means of the siphon which left the zinc granules in the bulb. The upper part of the rectification tube was dried again, etc. The receiver was dried by centrifuging and using the suction pump.

The whole procedure is very simple but it will be necessary to practice it a few times with an ether solution of known concentration before putting it to actual use.

Results

The results shown in Table I have been obtained with ether solutions of known composition.

Table I. Isolation of Ether

Solution Taken	Ether Calculated	Ether Found	Error	Remarks
Cc.	*Mg.*	*Mg.*	*Mg.*	
About 50	44	37	−7	Ether added directly from pipet to 50 cc. of water in rectification flask
About 50	73	65	−8	
About 50	95	83	−12	
About 50	162	155	−7	
About 50	232	225	−7	
About 50	323	309	−14	
50	111	99	−12	Various standard solutions
70	70	63	−7	
60	43	33	−10	Standard 1 freshly prepared
60	43	32	−11	
60	43	37	−6	
60	43	37	−6	Standard 1 after one night in ice box
60	43	36	−7	
20 + 40 water	14	7	−7	
			−9	Average
60	43	31	−12	Standard 1 after one week standing at 20° to 28° C.
60	43	31	−12	
60	43	29	−14	

The (anhydrous) ether was always weighed in sealed pipets with long capillary ends. For the preparation of standard solutions the volumetric flask was three-quarters filled with ice water. Then the pipet with the weighed ether was dropped into the flask in order to break the lower point of the pipet. The upper end projecting from the opening of the flask was then cut open to permit the ether to flow out. Finally the capillary pipet was rinsed with ice water into the volumetric flask. The volumetric flask was filled up to the mark with ice water, the opening closed with a good cork, and the contents thoroughly mixed. The standard solutions were always kept in corked volumetric flasks with long narrow necks. Every time before taking a sample the contents were thoroughly mixed.

The last three series of experiments shown in the table indicate that no ether is lost if the solution is kept in an ice box. Even when standing for 7 days at a temperature near the boiling point of the ether, the loss is rather moderate.

The loss of ether on pouring from one vessel into another was demonstrated by the following experiments:

Sixty cubic centimeters of a solution of 43 mg. of ether were poured from a beaker from a height of 20 cm. into another beaker and back again. This was repeated five times and the ether content was then determined.

1. Room temperature, 24° C.; temperature of the solution, 3° C. Ether found, 27 + 9 mg.; loss on pouring, 7 mg.
2. Room temperature, 28° C.; temperature of the solution, 28° C. Ether found, 13 + 9 mg.; and in a second experiment 12 + 9 mg.; loss on pouring, 20 mg.

The experiments show that ice-cooled ether solutions may be handled without too much loss of ether. The results of these determinations have been corrected by adding 9 mg. of ether. This correction is justified by the fact that there is a constant error of −9 mg. of ether on an average, as may be seen from the table. This error is mostly due to the fact that a small droplet of ether always remains behind in the lower part of the narrow tube *h*. A small part of the ether is lost for the following reason: At the start of the experiment the rectification flask is filled with air mixed with some ether vapor. While the larger portion of the latter will condense in the receiver, a simple calculation shows that despite the low vapor pressure of the ether at the temperature of the acetone–solid carbon dioxide mixture (probably less than 1 mm. of mercury), it is sufficient to permit the volume of air contained in the flask above the solution (about 60 cc.) to carry away a small amount.

This latter error is especially serious in the case of distillations of ether solutions with the usual distilling apparatus (Liebig condenser) and explains why quantities up to 1 or 2 grams of ether may be completely lost if the escaping air is not forced to pass through ice-cooled water. (The condenser tube should go down to the bottom of the receiving vessel and the latter should be filled with small pieces of ice.) The danger of losing ether is greatest at the time when the contents of the distilling vessel are just beginning to boil.

The same considerations apply, of course, to steam distillations used for the recovery of ether (or other liquids of low boiling point) from biological material. It is also evident that great care must be taken in the preparation of the sample (cutting up of biological material). The source of the material should be thoroughly chilled, preferably with solid carbon dioxide, before the sample is removed. If this is impossible, as in the case of living animals or humans, the sample should, as pointed out by Haggard (*3*), be drawn directly into a vessel which may be quickly and tightly stoppered and immediately cooled.

Summary

A method for the quantitative determination of ether, by means of a modification of the rectification flask described by the authors in a previous paper, is presented. The ether is isolated as such by distillation and collected in a receiver cooled with an acetone–solid carbon dioxide mixture which also freezes out the water vapor coming with it. The subsequent centrifuging of the receiver effects the separation of the liquid ether from the ice and collects the ether quantitatively in the calibrated part of the receiver, where the volume of the ether is read directly after warming to room temperature.

The procedure has been tried out with solutions containing from 10 to 300 mg. of ether in 60 cc. of water and showed a constant error on an average of −9 mg. of ether. The method is extremely simple and requires no reagents besides acetone and solid carbon dioxide. A determination may be carried out within 15 to 20 minutes. The precision of the method is in agreement with the magnitude of error to be expected, due to loss of ether in the handling of the sample previous to the actual determination, even though the sample is prepared under the most favorable practical conditions.

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Rapid Quantitative Determination of Mercaptans

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In the course of recent investigations involving the use of copper soaps, it was observed that the gradual addition of a kerosene solution of cupric oleate to a sample of gasoline containing mercaptans was attended by decolorization of the dark green oleate solution and formation of a pale yellow gelatinous precipitate, followed by the production of a distinct green coloration in the solution as soon as a slight excess of the oleate had been added. This observation at once suggested a possible rapid method for the quantitative estimation of mercaptans. Previous methods reported in the literature have a number of serious drawbacks where their use for routine determination of the mercaptan content of cracked gasolines is concerned. The lamp method of Youtz and Perkins (*5*) and Faragher, Morrell, and Monroe (*2*) is indirect and moreover cannot give as accurate results for amounts of sulfur less than 0.005 gram, which are just the values of practical interest. The iodometric method of Sampey and Reid (*4*), while undoubtedly capable of giving very accurate results in an inert solvent, is useless in the presence of unsaturated hydrocarbons, as is the mercuric chloride method reported in the same paper. The excellent method of Borgstrom and Reid (*1*), involving titration with silver nitrate, while capable of giving very accurate results and apparent freedom from interfering materials, requires very careful manipulation and prolonged agitation to preclude high results.

The method described in this article has shown an accuracy comparable to that of Borgstrom and Reid, freedom from interference by materials normally encountered in a cracked gasoline with the exception of hydrogen sulfide, and the advantage of rapidity and simplicity of operation, an average determination taking only 2 to 5 minutes. The completeness of the reaction has been demonstrated even in the case of Cross-cracked gasolines from Coastal crudes, which would contain most of the mercaptans ordinarily encountered.

Materials

The individual mercaptans used in this investigation were *n*-butyl, isobutyl, isoamyl, heptyl, benzyl, and *m*-thiocresol, obtained from the Eastman Kodak Company and used as received without purification. Some were of indefinite age and exposure, accounting for their low purity as determined. Tests were also run on untreated Cross-cracked gasoline. The Ranger naphtha used in making up the mercaptan solutions had the following properties:

A. P. I. gravity at 60° F. (15.6° C.)	54.5
Initial boiling point	221° F. (104.4° C.)
Final boiling point	398° F. (203.3° C.)
Peroxides	None
Free sulfur	Trace

Solutions

Cupric Oleate. Titrations were carried out with a crude cupric oleate solution prepared by exact neutralization of elaine oil with sodium hydroxide, precipitation in warm dilute solution with approximately the theoretical amount of cupric nitrate, and purification by washing the coagulated cupric oleate. This was found to give a material having a more intense color than that prepared from pure oleic acid. The solution was prepared with kerosene free from oxidation products to contain about 4 grams of copper per liter. Standardization was accomplished by shaking a given volume

with dilute hydrochloric acid to remove the copper, which was then determined iodometrically. The standard solution is fairly permanent if kept in the dark, showing no alteration over a period of three months, and may be used as long as it remains clear and does not develop peroxides. A solution a year old exhibited a whitish precipitate and possessed a pronounced oxidized odor. Solutions of copper soaps other than the oleate may be used, if the reaction with the mercaptans goes to completion with sufficient rapidity and they have sufficient color to make the end point clearly visible. The reaction involves the reduction of the copper to the cuprous form with the production of cuprous mercaptide and organic disulfide and liberation of fatty acid:

$$4RSH + 2Cu(Ol)_2 = 2CuSR + R_2S_2 + 4H(Ol)$$

From this equation it follows that 1 Cu ≈ 2 mercaptan S.

Naphtha. The mercaptans were weighed by difference from a Lunge pipet directly into a weighed amount of Ranger naphtha and accurately measured volumes of this mixture were diluted with the same naphtha to the 50-cc. volume used throughout in the tests. The standard solutions were kept in the dark until used.

Method of Analysis

A definite weight or volume of the gasoline is placed in a glass-stoppered cylinder and the cupric oleate solution is added from a buret in small portions, with shaking. The end point is a pale green color, clearly visible even in the presence of considerable precipitate. It may readily be substantiated by filtering on an ordinary dry filter paper. Addition of 0.05 cc. of the oleate solution at the end point is sufficient to impart a distinct green tint to the gasoline when viewed in a layer of reasonable thickness. For a blank, a sample of the same type of gasoline should be sweetened—for instance by alcoholic caustic—and titrated to the same depth of color. This value usually ranges from 0.10 to 0.15 cc. of the oleate solution, and is subtracted from the mercaptan titration. The percentage of sulfur is then:

$$\frac{(\text{cc. Cu oleate} - \text{blank}) \times \text{grams Cu/cc.} \times 1.009 \times 100}{\text{wt. of sample}} = \%\ \text{mercaptan sulfur}$$

Further work is being done on the application of the method to dark-colored cracked distillates or oils. Preliminary tests, based on extraction of the mercaptans with alcoholic caustic with subsequent decomposition of the alkali mercaptides in the presence of clear naphtha by means of acid and titration of the washed naphtha, have shown a recovery of about 85 per cent of the mercaptan present. Losses are largely due to the ease of oxidation of the alkali mercaptides, and it is hoped that, by reduction of the naphtha extract with zinc dust and acetic acid in the usual manner before titration, more nearly theoretical results may be obtained.

Effect of Possible Interfering Substances

Addition of free sulfur to a standard mercaptan solution had no effect on the titration.

In the presence of hydrogen sulfide a dark brown precipitate of copper sulfide is produced, which obscures the end point. As pointed out by Borgstrom and Reid (*1*), hydrogen sulfide may be removed without seriously altering the mercaptan content by shaking with acidified cadmium chloride solution (*2*).

Addition of phenol or *o*-cresol to standard mercaptan solutions was without effect on the titrations.

Addition of crude petroleum acids or purified naphthenic acids to standard mercaptan solutions did not alter the titrations. In fact, a copper naphthenate solution appears perfectly feasible as a titrating agent.

Carbon disulfide was without influence on the titration.

Addition of octylene (Eastman Kodak Company) to a standard mercaptan solution apparently caused a low result. This was traced to the presence of peroxides in the octylene. Purified octylene was without any effect.

Organic disulfides have no effect on the titration.

Organic peroxides would not be present in a solution containing mercaptans, but might develop in the copper oleate solution because of the pronounced catalysis of oxidation reactions by copper salts. As was expected, addition of a gasoline rich in peroxides to some of the copper oleate solution and utilization of this mixture to titrate a standard mercaptan solution led to a decidedly lower titration than normal. This emphasizes the precautions to be observed with respect to the standard copper solution. The solution may be tested by shaking a few cubic centimeters with potassium iodide solution, when no pronounced iodine coloration should develop in the aqueous layer.

Results

Table I shows the figures obtained on titrating varying percentages of mercaptans in naphtha solution, the theoretical sulfur content being based on the weight of added mercaptan, assuming it to be 100 per cent pure. The last column shows the apparent actual purity of the mercaptan based on the consumption of copper. These figures show fair agreement among themselves for all except extremely low percentages of sulfur.

Table I. Determination of Purity of Mercaptans in Naphtha Solution by Titration with Copper Oleate

(50 cc. of naphtha used)

Mercaptan	Sulfur Theoretical		Sulfur Determined		Apparent Purity of Mercaptan
	Gram	%	*Gram*	%	%
n-Butyl (old)	0.0142	0.0382	0.0132	0.0354	92.7
	0.00285	0.00764	0.00254	0.00682	89.2
	0.0142	0.0382	0.0131	0.0352	92.0
n-Butyl (new)	0.00467	0.0125	0.00447	0.01197	95.7
	0.00934	0.0250	0.00894	0.0240	94.8
	0.000280	0.00075	0.000212	0.00057	74.7
	0.00280	0.00750	0.00255	0.00684	91.2
	0.0233	0.0625	0.0227	0.0608	97.4
	0.00186	0.00500	0.00170	0.00457	91.5
	0.00467	0.0125	0.00447	0.01197	95.7
Benzyl	0.00447	0.01198	0.00425	0.01140	95.1
	0.00894	0.02396	0.00858	0.0230	96.0
	0.001785	0.00478	0.00157	0.00422	88.1
	0.000357	0.000957	0.000298	0.000799	83.6
	0.01788	0.0479	0.0171	0.0458	95.7
Isoamyl	0.0118	0.0317	0.00902	0.0242	76.3
	0.0118	0.0317	0.00902	0.0242	76.3
	0.00590	0.0159	0.00455	0.0122	77.1
	0.0295	0.0791	0.0224	0.0601	76.0
	0.0118	0.0317	0.00880	0.0236	74.6
	0.0150	0.0403	0.01113	0.0299	74.3
	0.0150	0.0403	0.01135	0.0305	75.7
Isobutyl	0.00977	0.0262	0.00944	0.0253	96.7
	0.00977	0.0262	0.00944	0.0253	96.7
	0.02438	0.0654	0.02324	0.0624	95.4
	0.00977	0.0262	0.00922	0.0247	94.4
m-Thiocresol	0.00956	0.0256	0.00795	0.0213	83.2
	0.00956	0.0256	0.00795	0.0213	83.2
Heptyl	0.00738	0.01978	0.00702	0.01881	95.1
	0.01846	0.0495	0.01792	0.0481	97.2

Recalculating the first two columns on the basis of the approximate determined purity, the average absolute error over a range of 0.0007 to 0.06 per cent of sulfur is only about 0.0002 per cent, which far surpasses the accuracy of any other method so far published. Checks between different operators with different standard solutions fall well within 0.001 per cent. The naphtha tested after each titration was found to be doctor sweet.

In order to substantiate the presence of disulfides in the original mercaptans, which would account for less than 100 per cent purity, certain standard solutions were extracted

with alcoholic caustic to remove mercaptans, the residual disulfides were reduced with zinc dust and acid, and the mercaptans thus produced were titrated in the usual manner. The results shown in Table III, although only approximate, because of losses encountered during the reduction (evolution of hydrogen sulfide, etc.), indicate the actual purity to be approximately as indicated by the oleate titration.

Table II. Determination of the Accuracy of the Oleate Method

(50 cc. of naphtha used)

Mercaptan	Approximate Purity by Oleate	Mercaptan Sulfur Based on This Purity		Mercaptan Sulfur Determined		Difference in Sulfur Determined
	%	Gram	%	Gram	%	%
n-Butyl (old)	92	0.0131	0.0351	0.0132	0.0354	+0.0003
		0.00262	0.00703	0.00254	0.00682	−0.00021
		0.01305	0.0351	0.0131	0.0352	+0.0001
n-Butyl (new)	95	0.00443	0.01188	0.00447	0.01197	+0.00009
		0.00887	0.0238	0.00894	0.0240	+0.0002
		0.000266	0.00071	0.000212	0.00057	−0.00014
		0.00266	0.00713	0.00255	0.00684	−0.00029
		0.0222	0.0594	0.0227	0.0608	+0.0014
		0.00177	0.00475	0.00170	0.00457	−0.00018
		0.00443	0.01188	0.00447	0.01197	+0.00009
Benzyl	95.5	0.00427	0.01142	0.00425	0.01140	−0.00002
		0.00854	0.0229	0.00858	0.0230	+0.0001
		0.001704	0.00457	0.00157	0.00422	−0.00035
		0.000341	0.000914	0.000298	0.000799	−0.00011
		0.01707	0.0458	0.0171	0.0458	0.0000
Isoamyl	76	0.00897	0.0241	0.00902	0.0242	+0.0001
		0.00897	0.0241	0.00902	0.0242	+0.0001
		0.00448	0.0121	0.00455	0.0122	+0.0001
		0.0224	0.0601	0.0224	0.0601	0.000
		0.00897	0.0241	0.00880	0.0236	−0.0005
		0.0114	0.0306	0.01113	0.0299	−0.0006
		0.0114	0.0306	0.01135	0.0305	−0.0001
Isobutyl	96	0.00938	0.0252	0.00944	0.0253	+0.0001
		0.00938	0.0252	0.00944	0.0253	+0.0001
		0.0234	0.0628	0.02324	0.0624	−0.0004
		0.00938	0.0252	0.00922	0.0247	−0.0005
m-Thiocresol	83	0.00793	0.02125	0.00795	0.02130	+0.00005
		0.00793	0.02125	0.00795	0.02130	+0.00005
Heptyl	96	0.00708	0.01898	0.00702	0.01881	−0.00017
		0.01770	0.0476	0.01792	0.0481	+0.0005

Table III. Determination of Disulfides in Mercaptans

Mercaptan	Purity by Oleate Titration	Disulfide Sulfur by Reduction and Titration of Mercaptan Formed
	%	%
Isobutyl	96	3
Isoamyl	76	18.1
Isoamyl	76	16.4
Isoamyl	76	28.0 ($AgNO_3$ titration)

The nature of the reaction (*3*) was proved to be according to the formula:

$$4RSH + 2Cu(Ol)_2 = 2CuSR + 4H(Ol)$$

Filtration to remove the gelatinous precipitate and titration of the filtrate with alcoholic potash gave the theoretical titration for the calculated amount of oleic acid; reduction of the filtrate with zinc dust and acetic acid gave practically half of the original mercaptan figure; treatment of the precipitate with 1 to 1 hydrochloric acid liberated mercaptan; and treatment of the resulting copper chloride solution with sodium hydroxide produced a bright yellow precipitate indicative of a cuprous salt. The gelatinous nature of the cuprous mercaptide may be due either to the presence of oleic acid or to the fact that precipitation is entirely in the presence of a nonaqueous medium.

Comparison with Other Methods

For purposes of comparison the same mercaptan solutions were analyzed by the silver nitrate method of Borgstrom (*1*). Allowing only 15 minutes' shaking on back-titration of the excess silver nitrate, results up to 125 per cent of theory were obtained, as shown in Table IV. As stated by Borgstrom, this error is caused by silver nitrate occluded by the precipitate, which, in most cases, remains in the naphtha layer. On prolonging the period of shaking to 45 minutes, results more nearly in accord with the oleate titration were obtained. In the case of the lower mercaptans from Cross gasoline, the silver mercaptide remained in the aqueous phase and results checked the oleate titration almost exactly, from which it would appear that better contact between mercaptide and aqueous potassium thiocyanate solution had permitted more ready removal of occluded silver nitrate.

Table IV. Analysis of Mercaptan Solutions in Naphtha by Silver Nitrate and Iodine Methods

Mercaptan	Theoretical Sulfur for 100% Purity		Sulfur Determined		Apparent Purity	Per Cent of Purity as Determined by Oleate
	Gram	%	Gram	%	%	
			Borgstrom-Reid method			
Benzyl	0.00894	0.0240	0.00897	0.0240	100.2	105
Isoamyl	0.0118	0.0317	0.01170	0.0314	99.2	130
	0.0118	0.0317	0.01170	0.0314	99.2	130
	0.0118	0.0317	0.01180	0.0317	100.0	131
	0.0150	0.0403	0.01474	0.0395	98.3	129
	0.0150	0.0403	0.01296	0.0347	86.4	112
Isobutyl	0.00977	0.0262	0.01224	0.0328	125.3	130
	0.00977	0.0262	0.01169	0.0314	119.8	125
m-Thiocresol	0.00956	0.0256	0.00727	0.0195	76.0	92
	0.02388	0.0641	0.01885	0.0506	78.8	95
Heptyl	0.00738	0.0198	0.00828	0.0222	112.2	117
(Sulfur by oleate titration)						
Lower mercaptans from Cross gasoline	0.0107	0.0287	0.0108	0.0289	...	101
Higher mercaptans from Cross gasoline	0.0177	0.0474	0.0206	0.0552	...	116
			Iodine method			
m-Butyl	0.00467	0.0125	0.00471	0.0126	100.8	106
	0.0233	0.0625	0.0218	0.0585	93.2	98
Isobutyl	0.00488	0.0131	0.00487	0.0130	99.7	104
Isoamyl	0.0150	0.0403	0.01198	0.0322	79.9	105
	0.0150	0.0403	0.01174	0.0315	78.3	103
(Sulfur by oleate titration)						
Lower mercaptans from Cross gasoline	0.0107	0.0287	0.0118	0.0317	...	110
Higher mercaptans from Cross gasoline	0.0177	0.0474	0.0177	0.0474	...	100

In the titration of the isoamyl mercaptan solution by silver nitrate, it was found that practically no disulfide remained in the naphtha after filtering off the silver mercaptide, instead of the amounts shown in Table III. This observation was checked by addition of approximately four times as much butyl disulfide as mercaptan, titration of the mercaptan, removal of the mercaptide by filtration, reduction of the remaining disulfide and titration of the mercaptan formed. It was found that a quantity of disulfide sulfur approximately equal to the mercaptan sulfur had been removed from the solution, possibly by adsorption on the silver mercaptide. Further substantiation of this point will be sought at a later date.

A number of mercaptan solutions were likewise titrated by addition of excess standard iodine solution and titration of the excess with thiosulfate. The same difficulty was encountered as reported by Sampey and Reid (*4*) of a gradual return of the blue starch-iodine coloration after an end point had apparently been reached, with high results if the first figures were accepted. It was found that vigorous shaking for 20 minutes with gradual additions of a slight excess of thiosulfate gave an end point which was moderately permanent. Figures obtained in this way agreed quite closely with those obtained by copper oleate titration. Mercaptans from Cross gasoline were separated from the gasoline by

either aqueous or alcoholic caustic and again liberated in the presence of the Ranger naphtha. In this way, unsaturated hydrocarbons were removed. Phenols or cresols were, however, still present and, although partially corrected for by a blank, may have had some influence on the titration, accounting for the high result obtained on the lower mercaptans, which solution also contained the bulk of the phenols. All the above results are likewise shown in Table IV.

It appears that the copper oleate method possesses decided advantages over previously published methods. Its applicability to all types of mercaptans has not yet been established, but since doctor tests at the end of the various titrations have invariably shown the gasoline to be sweet, even in the case of Cross-cracked gasolines from Coastal crude oil, which would contain most of the mercaptans which should ordinarily be encountered, the method appears sufficiently accurate for normal plant control operation. It is planned to investigate the applicability of this method to the determination of disulfides by establishing a method of quantitative reduction to mercaptans. Further work will be undertaken as opportunity affords.

Acknowledgment

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Selenium in the Determination of Phosphorus and Nitrogen in Phospholipides

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Since Lauro (*2*) published his method using selenium as the catalyst in Kjeldahl determinations of nitrogen, several papers have appeared confirming his results and extending their application to additional materials. In this laboratory the method has been applied successfully to the determination of nitrogen in phospholipides.

As the digestion of phospholipides with selenium is carried out so smoothly, it was decided to see if this method could be used also in the analysis for phosphorus. It was found that the phosphorus values secured in this way were comparable with those obtained from a nitric acid–sulfuric acid digest.

Since both nitrogen and phosphorus values are usually desired in an analysis of phospholipides, the possibility of making both determinations from the same digest was investigated.

From Table I it is seen that the phosphorus can be determined satisfactorily from the residue of the nitrogen determination. The digestion, with selenium as the catalyst, takes place much more rapidly than if copper or mercury is used, and is more convenient than digestion with a sulfuric acid–nitric acid mixture. Time is saved in two ways: through the speed of the digestion with selenium, and through the determination of both nitrogen and phosphorus from the same digest.

Table I. Analysis of Phospholipides

	Phosphorus	Nitrogen
	%	%
	3.51	..
HNO_3-H_2SO_4 digestion	3.50	..
	3.53	..
	3.54	..
$CuSO_4$-Kjeldahl digestion	..	1.63
	..	1.64
	3.51	..
Se-Kjeldahl digestion with nitrogen analysis preliminary to phosphorus determination	3.51	1.63
	3.51	1.65
	3.53	..

The samples used for the above comparison were prepared by dissolving 8.6393 grams of commercial egg lecithin in carbon tetrachloride, diluting to 100 cc., and then pipetting off 10 cc. of the solution for each analysis. The sample for the selenium-Kjeldahl digestion was run into an 800-cc. Kjeldahl flask, 5 grams of potassium sulfate were added, and the solvent was evaporated off on the steam bath. Twenty cubic centimeters of sulfuric acid and 0.2 gram of selenium were added. On digesting, a clear solution was usually obtained in about 15 minutes, but the heating was continued for an additional 15 to 20 minutes. After cooling the solution, the nitrogen was determined in the usual manner. The residue from this determination was filtered while still alkaline to remove the precipitated selenium. To the filtrate, after acidification, about 30 grams of ammonium nitrate were added. The additional amount of ammonium nitrate over that recommended by the Association of Official Agricultural Chemists (*1*) was used to counteract the inhibiting effect of the high concentration of sulfate ion on the precipitation of the phosphorus. The phosphorus was precipitated from this solution, first as ammonium phosphomolybdate, and then as magnesium ammonium phosphate. The samples used as a standard of comparison were digested with 10 cc. of sulfuric acid and successive additions of 3-cc. portions of nitric acid until the solution became clear, after which the heating was continued 15 to 20 minutes. The phosphorus was precipitated from the digest in the same manner as outlined above.

The chief advantages offered by the determination of both nitrogen and phosphorus from the same digest are a saving of time and of materials. In research work on phospholipides, the progress of the purification of the material is often followed by determining the ratio of nitrogen to phosphorus. Not infrequently a rather small yield of the final pure product is secured. Under these circumstances the saving of the material being investigated would justify the use of this method of analysis.

This method of determining both nitrogen and phosphorus from a selenium-Kjeldahl digest has been tried only with phospholipides. However, it is likely that its application can be extended to other materials.

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Measurement of Viscosities of Liquids Saturated with Gases at High Pressures

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THE interest of the petroleum industry in increasing the yield of crude oil from producing formations has caused much thought to be given to the factors controlling its recovery. One of the most important of these appears to be the properties of the oil itself. Previous investigators found that dissolving natural gas in crude oil had a surprising effect on many of its physical properties. A general study of these changes was undertaken at the California Institute as Research Project 37 of the American Petroleum Institute. This paper describes the viscometer developed for the study of the effect of dissolved gas on the viscosity of crude oils.

Instrumental Requirements

In order to duplicate in some measure the range of conditions found in petroleum formations, saturation pressures up to 200 atmospheres (2940 pounds per square inch) and temperatures ranging from 20° to 95° C. (70° to 200° F.) must be attained. The work of other investigators (*1*), at lower pressures, indicated that the change in viscosity of the oil would be very large at saturation pressures of 200 atmospheres. An instrument is therefore required which will measure accurately a wide range of viscosities without requiring intermediate alterations or readjustments. There are several other requirements which must be met by an instrument suitable for this study. Some means must be provided for establishing equilibrium between the gas and oil within a reasonable time. The instrument should be of such a nature that its calibration is independent of pressure. There is also need for means of measuring the saturation pressure and of maintaining the temperature of the viscometer constant during a given set of measurements.

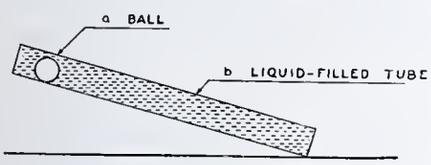

Figure 1. Diagram of Ball and Tube

Principle Utilized

The instrument which was found to satisfy most nearly the needs of this work was a modified form of the viscometer developed by Flowers (*3*) and Hersey (*4*). The sketch in Figure 1 illustrates the principle of the instrument. The ball *a* is at the upper end of the closed, liquid-filled tube *b*. As the ball moves down the tube (probably by both rolling and sliding), the displaced liquid must flow past it through the space between the ball and the tube. For any given ball with the tube held at a constant angle, the travel time of the ball multiplied by the difference between the density of the ball and that of the liquid is a linear function of the absolute viscosity of the liquid. This linear function breaks down, however, if the rate of movement of the ball is so great that the flow becomes turbulent.

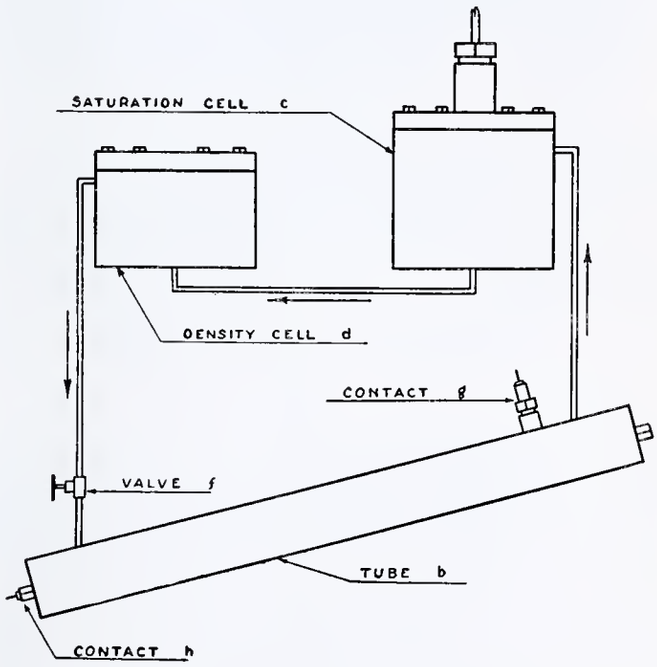

Figure 2. Diagram of Viscosity-Measuring Apparatus

Figure 3. Photograph of Instrument

The Instrument and Its Operation

Figure 2 is a sketch of the instrument developed upon the above principle. In order that equilibrium between the gas and oil may be reached, a closed circulating system is provided. The liquid flows from the saturation cell *c* to the density-measuring bomb *d*, thence to the bottom of the inclined tube *b* of the viscometer itself, returning from the top of the tube to the gas space of the saturation cell again. A small cam pump in the bottom of the saturation cell circulates

the oil through the system as desired. A photograph of the actual instrument is shown in Figure 3.

The entire system, except the upper part of the saturation cell, is filled with the oil sample, the system being so arranged that any entrapped gas is swept out upon circulation. Liquid is pumped through the system after thermal equilibrium is

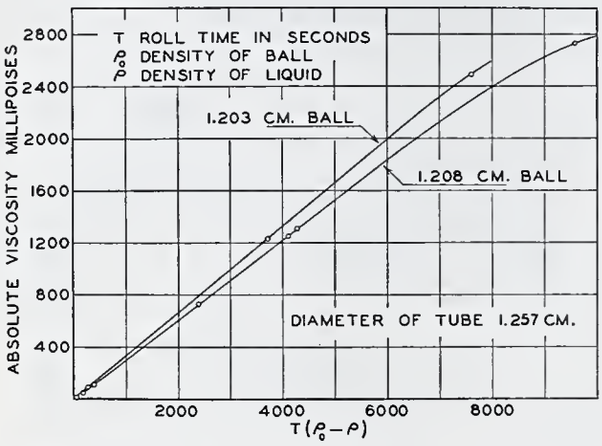

Figure 4. Calibration Curves for Two Balls

attained, the ball being forced to the upper end of the tube *b* above the outlet tube. When circulation is stopped, the ball is allowed to move part way down the tube. The upper contact *g* is then screwed down a small amount, and the circulation again started. The ball, moving up the tube, now wedges itself against the lowered contact, and is in position to start a measurement. This procedure of wedging the ball from below the contact gives a sharper and more reproducible release upon raising the contact than is the case with the ball above. The valve *f* at the lower end of the ball tube is now closed and the contact lifted, starting the ball down the tube. The break in contact is recorded on a chronograph. When the ball touches the lower contact *h*, another mark is made on the chronograph record. The valve *f* is again opened, circulation reëstablished, and the measurement repeated as often as desired. Next, gas is admitted to the top of the saturation cell and circulation maintained until the attainment of equilibrium is indicated by constancy of pressure reading. A new set of ball times is determined as before, more gas is then admitted, and the measurements are repeated at the resulting higher saturation pressure. This process is continued until the pressure approaches the upper limit of 200 atmospheres (2940 pounds per square inch). A series of determinations of this nature involving measurements at ten different pressures requires in the neighborhood of two hours after the initial thermal equilibrium has been reached.

The density of the liquid is measured in the density bomb at each of the saturation pressures by means of a small torsion-mounted balance. Since the two ends of the beam are constructed of materials of different density, the volume displaced is different and the force required to bring the beam into balance is a function of the density of the liquid in which it is immersed. This force is supplied by two solenoid coils, one mounted on the beam, and the other held in a fixed position. When current is passed through the coils a repelling force is exerted between them. By measuring the current flowing through the coils when the beam is in balance, a measure of the density of the liquid in which the beam is immersed is obtained. The instrument is calibrated by immersing it in a series of liquids of known density.

The saturation pressures are measured by means of a fluid pressure scale connected to the gas space of the system through a mercury trap. The trap is necessary to prevent contamination of the gas by the oil used in the fluid pressure scale. The temperature of the viscometer is held at any predetermined value by means of an oil bath controlled by a mercury regulator. The temperature of the bath can be varied between 20° and 95° C. (70° and 200° F.); the maximum variation from the desired temperature during a run is about 0.03° C. (0.05° F.).

Calibration

The viscometer is calibrated by measuring the roll time at atmospheric pressure for liquids of known viscosity. The liquids used in this work were standardized by the Bureau of Standards. The viscosities of these liquids were known at several temperatures, so that the effect of temperature on the calibration of the instrument could be determined.

Figure 4 shows calibration curves for two balls of slightly different sizes. The curves are straight lines over the greater part of the range but flatten off at roll times over twelve to fifteen minutes. This may be due to the break-down of the film between ball and tube. The effect of turbulence can be seen at the short roll times on the upper curve. The instrument gives satisfactory results in this range if enough calibration liquids are used to give the location of the curve with the desired certainty. The marked divergence of the two curves for a small change in ball size points to the need of high accuracy in the machining of both the ball and the tube. It is also evident that change in the surface condition of either the ball or the tube will change the calibration of the instrument to a marked extent. The balls used in this work were spherical to within 0.0001 inch, this degree of accuracy being necessary to obtain duplication of roll times of 0.25 per cent.

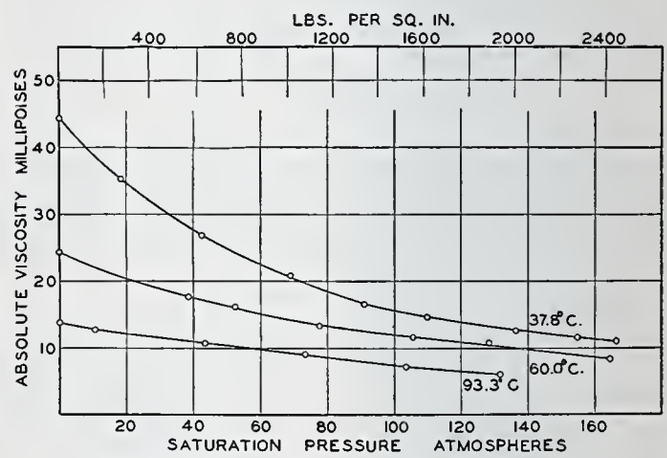

Figure 5. Viscosity Curves at Different Temperatures

The effect of pressure on the calibration of the instrument was investigated by comparing the small measured increase in viscosity of water under pressure with that expected from the work of Bridgman (*2*). This comparison indicated that at 170 atmospheres (2500 pounds per square inch) any change in calibration due to pressure could be neglected.

The range of measurable viscosities covered with one ball is quite large, from about 2500 millipoises down to 10 millipoises. However, the long roll times encountered at the higher viscosities make a smaller ball desirable when working in this range.

From the measured roll time and the density of the liquid, it is a simple matter to read the absolute viscosity from the calibration curve. The kinematic viscosity can then be computed from the absolute viscosity and the density.

An illustrative set of results is shown in Figure 5. These

viscosity curves are for a sample of Santa Fe Springs oil and dry natural gas at three temperatures. The decreased effect of the dissolved gas at the higher temperatures is probably due to the lower solubility of the gas under these conditions.

Conclusions

The use of this instrument has indicated that:

1. The viscometer described may be satisfactorily applied to the study of the effect of dissolved gas upon the viscosity of crude oil at relatively high pressures.
2. The instrument is satisfactory for use at temperatures up to 100° C. (212° F.).
3. A wide range of viscosities can be measured with one ball, and to extend such range greatly, only a simple change of ball sizes is needed.
4. Both the ball and the tube must be made with a high degree of accuracy.
5. The density of the liquid must also be measured in order to arrive at either the kinematic or the absolute viscosity.

Acknowledgment

This instrument was developed as part of Research Project 37 of the American Petroleum Institute. Financial support for this work has been received from a fund given jointly by John D. Rockefeller and the Universal Oil Products Company. Credit is due W. N. Lacey for his suggestions and interest in the design of the instrument. Charles Kircher did much to aid in the construction and the operation of the instrument. Acknowledgment is made to Harvey T. Kennedy, of the Gulf Research and Development Corporation, Pittsburgh, Pa., for his suggestion of an improved method of plotting calibration curves.

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Use of a Selenium–Mercuric Oxide Combination in Determination of Nitrogen in Feed Materials

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In 1931 Lauro (*2*) reported that the time required for digestion of the sample in the Kjeldahl method for the determination of nitrogen can be materially reduced by the substitution of selenium oxychloride for the more commonly used catalysts, copper and mercury, or their compounds. Since then a number of papers have appeared (*3–6*) in which the authors have given the results of comparative studies of the efficiency of various catalysts, or combinations of catalysts, in the reduction of the time required for complete digestion. The data thus far reported have, for the most part, been obtained in analyses of cereal grains or their products and are somewhat at variance. This laboratory has had occasion in the past to investigate the efficiency of metallic selenium in the Kjeldahl determination of nitrogen in materials commonly used in animal feeds, and the data presented herein may prove of interest to laboratories engaged in similar work.

A series of analyses was made in which the relative catalytic efficiencies of mercuric oxide, metallic selenium, and a mercuric oxide–selenium combination were compared. The Kjeldahl-Gunning-Arnold method (*1*) was followed, the digestion times being varied from 30 to 90 minutes. In the case of the mercuric oxide and selenium comparisons 1-gram samples of the materials were analyzed with the usual amounts of sulfuric acid and sodium sulfate, together with the addition of 0.7 gram of mercuric oxide or 0.15 gram of powdered selenium. The mercuric oxide–selenium catalytic combination was added in the form of a flux modified slightly from that described by Messman (*3*): 100 parts of sodium sulfate ($Na_2SO_4 \cdot 7H_2O$), 7 parts of mercuric oxide, and 1.5 parts of selenium. Ten grams of this flux were added to a 1-gram sample. All digestions were started on cold 600-watt burners.

Table I presents the data obtained.

It will be observed that, with the exception of the wheat bran and wheat shorts, the percentage of nitrogen obtained after 30 minutes' digestion in the presence of the mercuric oxide–selenium flux is in better agreement with that value obtained after 90 minutes' digestion with mercuric oxide alone, than are the nitrogen percentages obtained when mercuric oxide or selenium, alone, was used with an equal digestion time. These data are therefore in agreement with those of Osborn and Krasnitz (*4*). No significant differences exist between the relative efficiencies of mercuric oxide and selenium when each is used alone. This fact is also in accord with findings of previous investigators (*4, 6*).

Table I. Results of Comparative Analyses

Material	Catalyst	Nitrogen Determined			
Time of digestion		30 min.	45 min.	60 min.	90 min.
		%	%	%	%
Cottonseed meal	HgO	6.80	6.91	6.95	6.94
	Se	6.86	6.90	6.94	6.93
	HgO-Se	6.90	6.96	6.94	6.94
Corn oil meal	HgO	3.71	3.71	3.77	3.78
	Se	3.70	3.75	3.74	3.77
	HgO-Se	3.75	3.76	3.78	3.76
Linseed meal	HgO	5.79	5.83	5.84	5.86
	Se	5.81	5.82	5.84	5.84
	HgO-Se	5.82	5.84	5.87	5.87
Wheat bran	HgO	2.57	2.59	2.60	2.62
	Se	2.58	2.59	2.59	2.60
	HgO-Se	2.58	2.62	2.62	2.62
Meat and bone scraps	HgO	8.62	8.73	8.74	8.80
	Se	8.65	8.72	8.71	8.81
	HgO-Se	8.72	8.74	8.78	8.76
Wheat shorts	HgO	2.87	2.89	2.91	2.90
	Se	2.87	2.88	2.89	2.90
	HgO-Se	2.87	2.90	2.90	2.90

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Handling of Distilled Water in Aluminum

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A PLENTIFUL supply of satisfactorily pure distilled water is a necessity in modern chemical laboratories. Provision of such a supply entails consideration of the still to be used and the storage and distribution of the water.

Factors involved in the selection of a still include capacity of still, preference as to means of heating, ease of cleaning, maintenance, and operation, and, most important of all, the quality of distilled water which the still will deliver when fed with available raw water. This latter factor is often overlooked, although there is admittedly a wide variation of still performance in handling different types of water. Still operation is an important factor in distilled water quality. The market affords a wide choice of stills and it is now possible, at reasonable cost, to provide laboratories with stills which deliver adequate amounts of suitably pure distilled water.

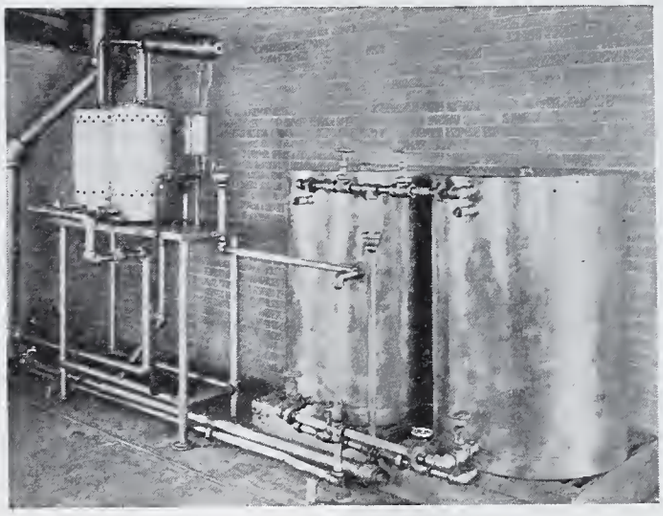


Figure 1. Equipment for Production and Storage of Distilled Water

Each aluminum tank holds 120 gallons, fittings are all aluminum, and distilled water is distributed through aluminum pipe lines

Storage and Distribution System

In planning a distilled water supply, the second step comprises the planning of the storage and distribution system. It is obviously absurd to produce satisfactorily pure distilled water and then contaminate it by improper handling. Consideration of a storage and distribution system at once raises the question of construction material. A satisfactory material for such purposes is one which is available in a variety of forms, reasonable in price, easy to fabricate and assemble, and, most important of all, which will not objectionably contaminate the distilled water to be handled.

Most of the laboratories of this country handle distilled water in block tin, in tinned copper, or in glass. Piping is usually in block tin, tankage and storage in tinned copper, and storage in glass. There are some shortcomings to all these applications. Block-tin pipe is usually assembled by soldering. Horizontal runs of pipe require support at close intervals. Glass containers are usually only of the bottle or carboy type and are rarely a permanent part of the storage system. Tinned copper has the disadvantage of being satisfactory only during the life of the tinned coating. An incident occurring a few years ago illustrates one of the hazards of tinned-copper storage tanks. Some aluminum powder had been sold on a specification that it should contain a maximum of 0.04 per cent copper. The customer received the powder and reported a copper content of 0.11 per cent. Investigation revealed the fact that if the customer's distilled water, in equivalent amount to that used in the analysis of the powder, were acidulated and electrolyzed, copper equivalent to 0.07 per cent in the metal was plated out. Thus there are problems to be solved in handling distilled water, even in what is accepted as standard material today. However, distilled water can be successfully handled in the materials discussed. Evidence is also available that another material —aluminum—is satisfactory.

Applicability of Aluminum

Except for very special purposes the water used in chemical laboratories is once distilled. It is apt to contain as much as 2 p. p. m. total solids. It is obvious that storage tanks, pipe lines, and accessories must have a low susceptibility to attack if this limit is not to be exceeded. Aluminum has this characteristic.

The applicability of a material for a particular use is best established by actually putting it to that use and observing its performance. Aluminum has been used to hold and convey distilled water for more than 15 years. Its performance is illustrated by the analytical results obtained on periodic samples taken from taps in laboratories of the Aluminum Research Laboratories at New Kensington, Pa. Illustrative data are offered in Table I.

Table I. Distilled Water from Aluminum System

Sample	Date Sampled	Total Solids *P. p. m.*	Aluminum *P. p. m.*
1	March 31, 1932	0.40	..[a]
2	April 6, 1932	0.50	..[a]
3	April 15, 1932	0.50	..[a]
4	May 17, 1932	0.40	..[a]
5	May 24, 1932	0.40	0.0087[b]
6	June 3, 1932	0.60	0.0059
7	June 6, 1932	0.60	..[a]
8	June 10, 1932	0.40	0.0248
9	June 14, 1932	0.30	..[a]
10	July 25, 1932	0.55	0.0047
11	July 30, 1932	0.45	..[a]
12	Aug. 20, 1932	0.65	0.0067
13	Sept. 9, 1932	0.81	..[a]
14	Sept. 20, 1932	0.55	0.025
15	Oct. 14, 1932	0.43	..[a]
16	Oct. 21, 1932	0.40	0.010
17	Nov. 5, 1932	0.54	..[a]
18	Nov. 12, 1932	0.51	0.012
19	Jan. 13, 1933	0.65	..[a]

[a] Aluminum not determined.
[b] Determined by procedure of Cox, Schwartze, Hann, and Unangst (*1*).

Spectrographic analyses show that the total residues are principally calcium salts which obviously are derived from still performance. For example, a typical spectrographic analysis of the total solids shown in Table I shows in decreasing order of abundance the presence of the following elements: calcium, magnesium, barium, silicon, aluminum, zinc, iron, copper, sodium, lead, nickel, strontium, silver, fluorine, and tin.

The importance of proper operation of stills is often not fully realized. In recent years the dissolved solids in many waters have increased on account of drought or semi-drought conditions. Unless increased bleeding of the still was resorted to, considerable priming occurred and water of poor quality was produced. Many waters tend to form scale readily. This, of course, reduces the efficiency of distillation as regards quantity of output and sometimes lowers quality. The actual performance of distilling apparatus is often overlooked in investigations of distilled water quality and undue

emphasis is given to the role of the storage and distribution system. The minor character which this latter role sometimes assumes was shown by the examination of a purportedly representative sample of distilled water from the tinned-copper and block-tin system of a well-known university. This water showed 12.3 p. p. m. total solids. Sodium was the predominant element present. Spectrographic analysis of the residue showed the following elements in decreasing rate of abundance; sodium, tin, calcium, aluminum, copper, iron, silver, nickel, zinc, barium, lead, magnesium, and strontium.

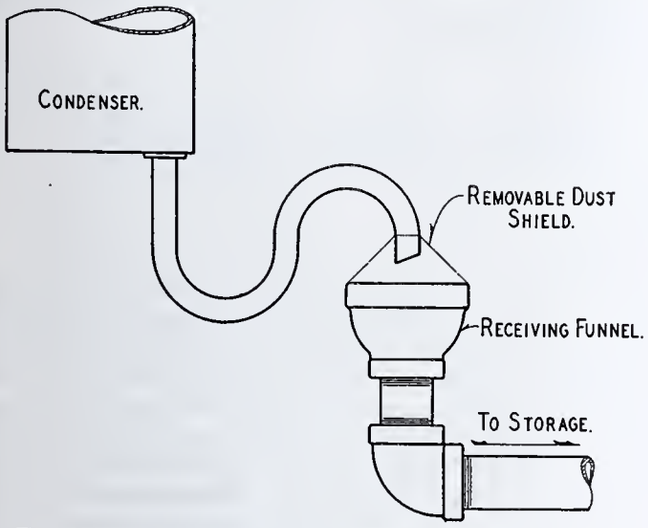


FIGURE 2. DETAIL OF ARRANGEMENT FOR AËRATION OF DISTILLED WATER

Distilled water from a tinned-copper, block-tin, and glass system in an industrial research laboratory showed 1.9 p. p. m. total solids. Spectrographic analysis showed calcium to be the principal element present, with the following elements in order of decreasing abundance: magnesium, sodium, aluminum, copper, silicon, nickel, manganese, zinc, iron, barium, tin, silver, strontium, and chromium.

Both of the two latter waters contained more aluminum than water from the aluminum system at the Aluminum Research Laboratories. With establishment of the fact that handling distilled water in aluminum does not materially contribute impurities to the water, we may pass to other considerations involved in the application of aluminum to the handling of distilled water.

Tanks for the storage of distilled water are formed from sheet. All seams are closed by autogenous welding. Threaded cast-aluminum inlet and outlet fittings are welded to the tank. The tubing and piping used for pipe lines are seamless tube or pipes. Fittings and valves are made of aluminum castings. Table II shows the recommended composition of metal for the various forms used.

TABLE II. NOMINAL COMPOSITION OF ALUMINUM ALLOYS FOR USE IN DISTILLED WATER SYSTEMS

APPLICATION	ALLOY[a]	COMPOSITION[b]
Storage	2S	99+% Al
Storage	3S	1.25% Mn
Storage	53S	0.7% Si, 1.25% Mg, 0.25% Cr
Pipe	2S	99+% Al
Pipe	3S	1.25% Mn
Pipe	53S	0.7% Si, 1.25% Mg, 0.25% Cr
Connections	43	5% Si
Connections	214	3.75% Mg
Valves	43	5% Si

[a] Alloy designations are Alcoa alloys of Aluminum Company of America.
[b] All alloys contain normal impurities; iron and silicon with small amounts of other elements.

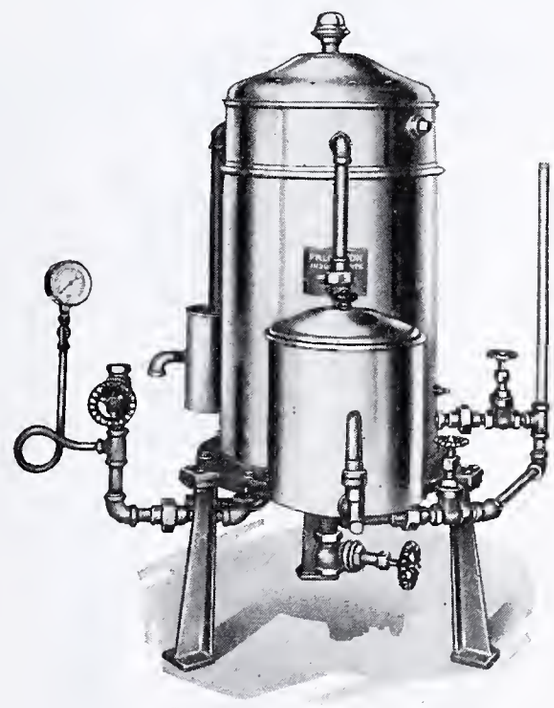
ASSEMBLY OF ALUMINUM SYSTEM

Assembly of the system is usually made by the use of threaded connections, though compression fittings or flanged connections of the Van Stone type are sometimes used. Care should be exercised to cut clean smooth threads. Just before assembly all threads should be examined to insure absence of residual cuttings or turnings or other foreign solid material.

Competent pipe fitters with experience in assembling other nonferrous piping should have no difficulty in aluminum pipe assemblies. Such work involves the avoidance of drawing up threaded joints too tightly. This is apt either to strip the threads or to cause the metal surfaces to gall or seize. The threads should be accurately engaged and the connection screwed up to the point where the operation entails some difficulty. In distilled water line assemblies it is suggested that lubricant be used sparingly and that "pipe dope" be not used. After the assembly is complete the line should be placed under a slight vacuum and all joints should be painted with shellac. This will effectively seal all joints but will not subsequently contaminate the water.

When the assembly is complete the entire assembly should be flushed out thoroughly with tap water. The entire system should then be filled with distilled water and allowed to stand for at least 12 hours. The system should then be drained and filled once more with distilled water and allowed to stand for at least 12 hours and then drained out. The system may then be filled with distilled water for use. Thereafter the system should require no particular attention.

The treatment with tap water and the subsequent treatment with distilled water have twofold functions: First, the interior surface is cleaned of all foreign material. Second,



Courtesy, Precision Scientific Company

FIGURE 3. ALUMINUM STILL

the aluminum becomes coated with an augmented coating of insoluble aluminum hydroxide which desirably coats the metal surface and eliminates the probability of further attack, even if distilled water of inferior quality is placed in the system.

The attack on most metals by water is accelerated by the presence of dissolved oxygen in the water. Aluminum is not one of these metals. It owes its corrosion-resistance to the adherent film of oxide on its surface. The presence of dissolved oxygen acts as a stabilizer of the film. If or when the film is broken or weakened the dissolved oxygen reacts to heal and strengthen the film. While not essential or necessary, it is wise to provide for some aëration of the distilled water supply. One method of accomplishing this may be

seen in the photograph of the water still and storage system of the Aluminum Research Laboratories (Figure 1). Figure 2 shows the detail of the arrangement whereby the distilled water discharged from the still condenser drops through air for a few inches before entering the storage system.

Additional evidence as to the satisfactory character of distilled water handled in aluminum systems is derived from an examination of blank determinations run in connection with analyses for R_2O_3 content. These blank determinations in the Aluminum Research Laboratories, which cover all reagents including distilled water used in analyzing the sample, never exceed 0.001 gram of R_2O_3.

Conclusions

The usefulness of aluminum for handling distilled water is shown by the fact that it does not seriously contaminate distilled water, it is available in a variety of wrought and cast forms, it is easy to erect and assemble, and the system may be easily disassembled in case such procedure is desirable.

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A Convenient, Inexpensive Water-Motor Stirrer

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Some elementary knowledge and experience in glass-blowing is desirable in constructing this motor stirrer. Two glass side arms *B* and *C* are attached to a 125- or 150-ml. Erlenmeyer flask *A*. The flask is closed with a one-hole rubber stopper carrying an arrangement of small glass tubing, similar to the familiar mercury seal, as illustrated at *D*. The glass stirring rod, extending through this stopper and seal, has a small stopper *G* attached to the upper end. This stopper *G* has inserted in slits in its upper portion small vanes of metal made of copper, aluminum, or similar metal, crossing at right angles as illustrated at *F*. A small glass jet *E* is introduced through the side arm at *B*, and held in place by a short length of rubber tubing. Suitable lengths of laboratory rubber tubing connected at *B* and *C* are added to carry the water to and from the flask. This entire arrangement is vividly shown in Figure 1. Figure 2 shows an end view from above of the arrangement of this jet *E* and the vanes for driving the stirrer.

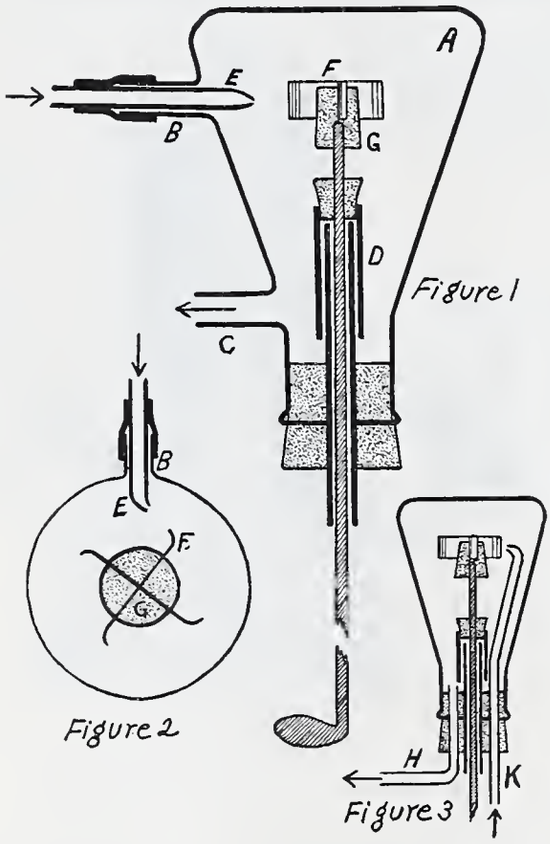

Figure 1

Figure 2

Figure 3

This stirrer is clamped to a ring stand with a small laboratory clamp with the flask in an inverted position as shown, when it is to be used. The stirrer is put in motion by merely introducing a stream of water from the usual laboratory outlet through the jet *E*. The waste water leaves the flask through *C*. It is desirable to have the outlet *C* larger than the intake at *B* to prevent the unnecessary accumulation of water within the flask. This stirrer will be found especially convenient for melting point baths and similar small containers. It may also be used with the usual organic reaction vessel or flask, even where it is necessary to attach an additional mercury seal at the mouth of the second reaction flask.

In case it is not convenient to attach the two side arms *B* and *C* to the small Erlenmeyer flask as illustrated in Figure 1, a three-hole rubber stopper may be substituted as illustrated in Figure 3. The stream of water enters through *K* and leaves through *H*. Otherwise the arrangement is the same. A wide-mouthed flask will permit a larger and more efficient type of construction in either case than the usual narrow-mouthed Erlenmeyer flask. In the type of construction illustrated in Figure 3 even a small wide-mouthed bottle may be used.

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Camphor. Approximately 60 per cent of the camphor produced in Japan during 1931 and 1932 came from the Island of Taiwan (Formosa), and the remaining 40 per cent originated in Japan proper, chiefly in the Island of Kyushu, according to information made available by the Department of Commerce. During the year ended March 31, 1931, the total production of crude camphor amounted to 4,585,568 pounds. In the following year the output dropped to 3,544,997 pounds. Camphor oil production totaled 17,275,246 pounds during the fiscal year 1930–31, and 15,921,621 pounds during the fiscal year 1931–32, the percentages of origin being the same as those of crude camphor.

Taiwan supplied a greater quantity of natural crude and refined camphor to Japan in the calendar year 1932 than in the preceding year, although the value declined markedly. Camphor oil also was obtained in larger amounts. Exports from Taiwan to Japan follow: camphor, 1931, 3,008,507 pounds; 1932, 3,138,202 pounds; camphor oil, 1931, 7,237,701 pounds; 1932, 8,403,116 pounds. Exports of camphor direct from Taiwan to the United States declined from 1,814,918 pounds in 1931 to 1,483,360 pounds in 1932, while shipments to other countries gained from 299,820 pounds to 580,346 pounds, respectively.

Increased exports of camphor from Japan proper occurred in 1932, the total amounting to 3,107,287 pounds, compared with 2,783,615 pounds in 1931. Shipments to the United States declined.

Nature and Constitution of Shellac

VII. Determination of Acid Number

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An accurate determination of acid number of shellac is a necessary prerequisite to the study of its behavior with respect to several of its applications. This is particularly true when studying shellac varnishes.

Some of the methods which have been developed for acid number cannot be accurately applied to shellac. These include the Albert method which has recently found wide use in this country for the general determination of acid numbers of resins. Results given in this paper show that for shellac it does not give true values. Partial hydrolysis of the alkali salts formed during the titration leads to a false end point with phenolphthalein, which is the only indicator that can be employed with this method.

The chemical constants of a substance, in the case of many natural materials, are one of the few means available for identification and in some instances the only method for estimating purity. Strictly speaking, in most cases the numbers obtained for unadulterated materials are not true constants, but represent ranges in properties by which the material may be characterized (*34*). It is unnecessary to stress the fact that the narrower the ranges the greater is their utility. The numbers representing these ranges might more correctly be referred to as "identification numbers," or "*kennzahlen.*"

A great deal of study has been given to the determination of the various values and numerous methods have been developed for each of these numbers. It has been the authors' experience (*32*), however, that in some instances methods which have been accurately developed for a specific substance have been generally applied to other materials without a complete study of the new applicability. The literature is filled with conflicting data (*6, 35*), which may in part be accounted for by the use of different methods.

Methods for Acid Numbers

In the determination of acid numbers a wide variety of methods and various modifications have been employed. In some cases a method has been developed to meet the peculiar characteristics of a particular substance, but even here there has been a tendency to make the method general. Since many of the methods used for resins were first developed for fats, oils, and waxes, it is desirable when considering methods for acid numbers of resins to include these latter substances.

The high coloration of the extracts of some of the substances, notably orange shellac, and the peculiar solubilities of other materials account to a large extent for the multiplicity of methods which have been developed (*6*). Even when employing the original method, which consists in titrating an alcoholic extract with alkali direct, numerous sets of directions are given.

Dieterich, who has made an extensive study of resins, recommends for storax (*7*) that a 1-gram sample be dissolved in 100 cc. of cold 96 per cent alcohol and titrated with 0.5 *N* alcoholic potassium hydroxide, using phenolphthalein as indicator. This method is very similar to the standard method adopted by the American Society for Testing Materials for linseed oil (*2*). Richmond, on the other hand, recommends the use of a solution of 1 gram in 50 cc. of absolute alcohol for manila copal (*23*), whereas Slack (*28*) prefers a 5-gram sample for fats, oils, and waxes and titrates with 0.1 *N* alcoholic alkali. Richter (*24*) uses 30 to 40 cc. of an equal mixture of absolute alcohol and ether with 1.0 *N* alkali for this purpose. Niegemann (*20*) recommends 0.2 *N* aqueous alkali and states that at least 2 cc. of a 1 per cent solution of phenolphthalein should be used. Gardner and Coleman (*10*, cf. *18*) point out that colloidal substances do not give true acid numbers when determined in the usual manner. For substances incompletely soluble in alcohol, they recommend a mixture of equal parts of alcohol and benzene, dissolving 1 to 2 grams in 40 cc. of the mixture, refluxing for 30 minutes, and allowing to cool before titrating with 0.1 *N* sodium hydroxide. Steel and Sward (*29*) have used this alcohol-benzene mixture for vegetable oils. Kettle (*13*), on the other hand, has employed a mixture of 90 per cent of benzene with 10 per cent of alcohol for oils. Singh (*27*) dissolves 1 gram of shellac in 100 cc. of boiling alcohol, refluxing for 5 minutes. He filters and cools before titrating with standard aqueous potash, using phenolphthalein as indicator. Parry (*22*) claims that the presence of lac dye in some samples obscures the end point with phenolphthalein. Kranz and Majrich (*14*) find that α-naphtholphthalein, alkali blue, and phenolphthalein are the most practical indicators for resins when titrated with 0.1 *N* potassium hydroxide. For shellac Nagel and Körnchen (*19*) recommend alkali blue 6R, using alcohol solutions. Whitmore, Weinberger, and Gardner (*32*) use thymol blue.

To overcome the inaccuracies caused by high coloration of solutions, Dieterich (*6*) has developed a method where the resin is dissolved in a standard amount of alkali and back-titrates with standard acid. The alkali serves both to neutralize the resin and as a solvent. The method cannot be used with substances which contain esters which are readily saponified. For dammar and sandarac (*8*) he dissolves 1 gram in 20 cc. of 0.5 *N* alcoholic potassium hydroxide, adds 50 cc. of benzene, and after standing for 24 hours titrates the excess with 0.5 *N* sulfuric acid. For ammoniacum a preliminary refluxing with water and alcohol for 15 minutes is recommended (*9*) and part of the filtrate is treated with 0.5 *N* alcoholic alkali. In this case only 5 minutes' contact is required before titrating with acid.

For similar reasons potentiometric methods have been employed. Kremann and Muss (*15, 16*) titrated fatty acids dissolved in alcohol with 0.5 *N* alcoholic sodium hydroxide in this manner; Seltz and McKinney (*26*) fatty acids and lubricating oils. Gardner and Whitmore (*11*) studied the applicability of the method to resins, including shellac; and Caldwell and Mattiello (*3*) linseed oil and its fatty acids. The latter authors found they could use successfully not only 95 per cent alcohol, but also butyl alcohol, and mixtures of equal volumes of alcohol and benzene as solvents. These methods are unquestionably the most accurate that can be employed, since they are totally free from inaccuracy in judging the end point of the indicators or due to color of the solution. They are not as convenient as the other methods, however, since the electrodes have to be carefully prepared (*3, 11*). For investigation purposes they are unexcelled, since the titration curves give at the same time considerable information concerning the nature of the material being titrated. By comparing results obtained by other methods with those obtained by the potentiometer, considerable improvement in technic and means of judging end points can be effected.

A fourth type of method for acid number is typified by the Albert method (*1*). Here the substance is dissolved in a 2-to-1 mixture of benzene and alcohol, and a two-layer system formed by the addition of a saturated aqueous salt solution. Aqueous alkali and acid are employed in the titration, using phenolphthalein as indicator. These methods have the advantage of giving a clear end point, since the phenolphthalein is retained in the aqueous layer while the resin and its salts remain in the upper organic solvents. The same end point may be obtained several times by adding a slight excess of alkali and back-titrating with

acid. Stock, who modified the original method to a slight extent, determined values for a variety of resins (*30*). It is clear from his value for shellac that he was not dealing with a usual sample. Coburn (*4*) with similar modification used this method for dark-colored samples of rosin. His values agree better than Stock's with these obtained by the usual method of titrating spirit solutions directly with alcoholic alkali.

It can be seen from this review that many of the methods which have been used differ widely both in technic and in principle. In only a few cases have attempts been made to compare results obtained by more than one or two methods, so that we are left in serious doubt when attempting to establish limits of variation for many substances, especially by consulting the literature for possible climatic variations over long periods of time. The adoption of standard methods and systematic recording of results in the literature are highly desirable. They have been accomplished to some degree in the case of some oils (*2*), but should be rapidly extended to include many other substances.

Acid Numbers for Shellac

The values given for shellac do not vary as widely as do many of those given for other substances, but in some instances the influence of method is obvious. Parker (*21*) obtained values of 60 and 66 for button and flake shellac; Williams (*33*) 47.6 to 64 for the same varieties and garnet. His widest variation occurs with the flaked variety. Kremel (*17*) obtained 63.5 for a yellow lac; Schmidt and Erban (*6*) values from 60 to 65; and Dieterich 59 to 63. Singh (*27*) used aqueous alkali for titration and obtained values of 60 to 65. His values are the only example of shellac derived from a recorded source. On drying or melting, he found that the values were reduced to 52 to 60. Umney (*31*) obtained values of 53 to 78 for all grades of shellac, and a value of 44 for stick-lac. Coffignier (*5*), using the conventional method, found 60 for shellac and 35 for stick-lac. Rudling (*25*) obtained 53 to 59 for seed-lac and button-lac, Parry (*22*) 55 to 65, and Ulzer and Defris (*6*) 65.4. Nagel and Körnchen (*19*) stated that the acid numbers of all grades range from 60 to 70 and for rosin-free samples 60 to 65. Gardner and Whitmore (*11*) showed values of 67.5 to 73; and Whitmore, Weinberger, and Gardner (*32*) 70 to 75. For bleached shellac Kremel (*17*) obtained 73.7, Coffignier (*5*) 81, Gardner and Whitmore (*11*) 85.7, and Whitmore, Weinberger, and Gardner (*32*) 93.6. For refined wax-free bleached shellac the latter authors obtained 107.5 to 117.6.

The general uniformity of results ranging between 60 and 65 may be due to the common use of alcohol solutions and phenolphthalein as indicator. The values which are lower than 60 almost invariably occur for the poorer grades of shellac and may in part be accounted for by difficulty in judging the end point, which is masked by the deep wine color of the alkali salt of the yellow dye erythrolaccoin present in the orange grades. It is also possible that in these grades the acid value has been reduced, as Singh (*27*) has shown, by excessive heat or drying. Since the resin content is given in only a few cases, it is difficult to judge what the true value should be (*32*). The higher range of values of Gardner and Whitmore is unquestionably due to the more accurate method employed in judging the end point.

Direct Method for Determining Acid Numbers of Shellac

It had been the previous experience in this laboratory that by following the potentiometric titration with outside indicators, for an accurate end point with phenolphthalein a fairly distinct pink must be taken. Because of the difficulty in judging such an end point, especially in the presence of the aforementioned dark purple color, the authors have substituted thymol blue as the indicator. Although the potentiometric titration curves show a sharp inflection for all grades of shellac, nevertheless even with thymol blue there is a slight range in color change from yellow through green to blue at the end point. From a comparison with fatty acids of similar acid strength it might be expected that both these indicators would show a rapid rate of color change. What is sometimes overlooked in change of solvents in a determination is that the indicator range may also be changed and not in the same proportion. It would appear that the use of 95 per cent alcohol depresses the range of alkalinity of the two indicators. By taking as the end point the first indication of a permanent blue with thymol blue when using two to three drops of a 0.04 per cent alcohol solution of the indicator on a spot plate with one to two drops of the solution, the authors have been able to obtain values which closely approach those obtained with the potentiometric method. This would account for the relatively higher results of Whitmore, Weinberger, and Gardner (*32*).

The exact method employed consists of the following:

Dissolve 5.000 grams of shellac, which has been carefully rolled, in 50 cc. of neutral 95 per cent ethyl alcohol. Titrate with standard 0.5 *N* alcoholic potassium hydroxide, using thymol blue (thymosulfonphthalein 0.04 per cent in 95 per cent alcohol) as outside indicator. A porcelain spot plate is convenient for this titration. The end point is taken as that point where one to two drops of the solution on a glass rod gives the first temporary blue coloration to the indicator. The alcoholic alkali should be standardized against aqueous acid each time before using to correct for any error in change in density due to fluctuations in temperature.

Identical results are obtained by this method when 50 per cent of benzene is added to the solution before titration. Since all the acid constituents of shellac are spirit-soluble, it is unnecessary to use any other solvent. At least 5 grams should be taken as a sample in order to obtain uniformity of material for duplicate determinations. Proper rolling of sample is very important. As can be seen from Table I, excellent checks are obtained with duplicate samples.

Table I. Influence of Amount of Benzene Used in Albert Method

Sample: T. N. orange shellac

Ratio $C_6H_6:C_2H_5OH$	Acid Number: Albert method	Acid Number: Weinberger-Gardner direct method
3:1	69.5	76.1
3:1	69.0	..
2:1	67.2	76.0
2:1	67.2	..
1:1	66.6	76.0
1:1	66.8	75.9
1:1	66.0	..
1:1	66.5	..
1:1	66.4	..
0:1	..	76.0

Indirect Method

Because of the somewhat greater ease in judging the end point of thymol blue when titrating with acid, an attempt was made to determine the acid number by the indirect method:

Dissolve 5 grams of shellac in 25 cc. of neutral alcohol, add 25 cc. of 1.0 *N* alcoholic potassium hydroxide, and titrate the solution immediately with 0.5 *N* alcoholic sulfuric acid.

As can be seen from Table II, this method gives high results. For confirmation that saponification takes place in such a rapid manner one sample was allowed 10 minutes' contact with the alkali before titrating. This raised the acid number by 20, and leaves no doubt as to the inapplicability of these methods to shellac.

Table II. Presence of Saponification in Indirect Method

Sample: Superfine (composite) orange shellac

Direct Method	Indirect Method
70.2	77.2
70.2	75.6
..	90.7[a]

[a] Titrated after standing for 10 minutes.

Albert Method

For reasons cited above, it is advisable to use at least a 5-gram sample of shellac. This procedure was followed when employing the Albert method, and in order to compensate for the larger sample the amount of solvents was increased. The determination was conducted in the following manner:

Dissolve 5.0000 grams of shellac in 100 cc. of a mixture of two parts of benzene and one part of alcohol. When solution has taken place, add 100 cc. of neutral saturated sodium chloride solution, with several grams of the solid salt and a few drops of phenolphthalein solution. Titrate the solution with 0.5 *N* aqueous sodium hydroxide with careful but thorough agitation. (Too vigorous agitation will cause the shellac to become wetted with water and adhere to the sides of the flask. A swirling motion was found to be the best.) Add hydroxide until the aqueous layer has a definite red color and then titrate with 0.5 *N* sulfuric acid until the pink just disappears. Repeat the addition of alkali and back-titration with acid until two or more consecutive readings give the same value for acid numbers.

Varying the amount of liquids did not affect the results. With seed-lac, the red lac dye present prevents the obtaining of an end point with phenolphthalein. Thymol blue and other indicators of this range were either affected by the saturated salt solution or showed too great a solubility in the organic layer to be effective. Attempts to remove the lac dye by the formation of an insoluble lake with soluble lead or barium salts were not satisfactory. The effect of changing the ratio of benzene to alcohol for orange shellac is shown in Table I. As can be seen, an increase in alcohol depresses the acid number.

A comparison of the values obtained by this method and those determined by the direct method is given in Table III. The numbers obtained by the Albert method are lower than those by the direct. They do not, however, show any constancy in difference.

Table III. Comparison of Direct and Albert Methods

Sample	Acid Number: Direct method	Acid Number: Albert method	Difference
T. N. orange	76.0	67.2	8.8
Heart orange	70.8	56.0	14.8
A. S. O. (special)	73.9	64.6	9.3
Bleached shellac	93.7	87.7	6.0
Seed-lac[a]	69.4	59.5	9.9
Palmitic acid	215.6	218.8	−3.2

[a] This sample contained very little lac dye.

In seeking an explanation for the results obtained with the Albert method, 5 grams of shellac were dissolved in alcohol and just neutralized with alkali by following the procedure in the direct titration method. Twice the amount of benzene was added to this solution, and then the saturated salt solution. Upon addition of phenolphthalein the aqueous solution was found to be alkaline. Back-titrating with aqueous acid gave a value identical with that originally obtained by the Albert method. From this it was clear that the difference in values was an inherent function of the two methods.

At first it was thought that the difference might be caused by a difference in range of end point of the indicators in the two different solvents, alcohol and saturated brine solution. However, the authors were able to show that by adding water to a neutralized alcoholic solution of shellac and boiling off the spirits, an aqueous solution neutral to both thymol blue and phenolphthalein was obtained. Addition of a drop of alkali to this solution rendered it alkaline to either of these indicators. By adding amyl alcohol to the neutral aqueous solution derived in this manner by the direct titration method, a two-liquid layer system is formed and the aqueous layer readily becomes alkaline.

By using filtered alcoholic solutions of shellac it can be demonstrated that clear aqueous solutions of the potassium salt of shellac can be obtained in this manner similar to those obtained with wax-free bleached shellac (*12*). Clear solutions, however, are obtained only if sufficient alcoholic alkali is added to correspond to the acid numbers obtained by the direct method. Since any free shellac is highly insoluble in water, these experiments would favor the contention that the higher acid numbers of Gardner and co-workers represent the truer values for shellac.

Conclusions

The results obtained by the Albert method might be explained in the following manner: Since it has been shown that shellac behaves as a weak organic acid (*11*, *12*), its potassium salts would have a tendency to hydrolyze in water. Because of the marked insolubility of shellac (acids) in water, this hydrolysis proceeds only to the normal degree in aqueous solution; however, when there is a two-liquid layer system in which shellac is very soluble in the organic layer, any free shellac which is formed as a result of hydrolysis will be removed from the aqueous layer and hydrolysis can proceed to a much greater extent:

Single-layer systems:

$$\text{Potassium shellacate} \longrightarrow K^+ + \text{shellac ions}$$
$$HOH \rightleftharpoons OH^- + H^+$$
$$\Updownarrow$$
$$\text{Shellac (solid)}$$

Two-layer system:

$$\text{Potassium shellacate} \longrightarrow K^+ + \text{shellac ions}$$
$$HOH \longrightarrow OH^- + H^+$$
$$\Updownarrow$$
$$\text{Shellac (solid)}$$
$$\downarrow$$
$$\text{Shellac solution (alcohol-benzene)}$$

When selecting a method for study as a standard for the acid number of shellac, extreme care should be taken to consider some of the peculiarities of this material. Because of its difference in source and nature, methods which may successfully apply to other resins will not necessarily give accurate results with shellac. It would appear from this study that only the group of methods known as the direct methods and the potentiometric methods are open to selection. In developing such a method, consideration should be given to the amount of sample taken for analysis, care of rolling, the neutrality of the alcohol, constancy of titer of alkali, proper selection of indicator, and standardization of method in judging end point.

Since this work was undertaken, the importance of acid numbers for shellac has become recognized in this country. Further study is in progress upon this subject.

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Glass Spheres for Viscosity Determination of Cuprammonium Solutions of Cellulose

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Large quantities of glass spheres, all of which have the same time of fall through a standard liquid, can be obtained by the method described herein. Since all these spheres have the same characteristics of fall in a given viscometer, they are particularly suited for those viscosity methods which require glass spheres, as, for example, cuprammonium solutions of cellulose.

The accuracy of the falling-sphere method for viscosity determination depends in a large measure on the degree of care exercised in the selection of the spheres used.

When metal spheres are used, this selection presents no difficulties because of the uniform gravity of metal and the precision to which such beads may be ground. In certain solutions, however, the use of practically all metals is prohibited, because of the corrosive nature of the solution, the high specific gravity of the metal, or the opacity of the bead. Since this is especially true of cuprammonium solutions of cellulose, glass beads should be used for such viscosity work.

In the standard method for the determination of the viscosity of cellulose as described by the Division of Cellulose Chemistry of the American Chemical Society (*1*), a bead of certain specifications is required. Glass beads when molded or blown are not uniform in shape, size, or specific gravity. The effect of these irregularities is overcome in the above method by calibrating each bead separately and reporting the viscosity in poises. This tedious procedure leads to the use of a large number of spheres, each of which may have a different centipoise rating. The use of such spheres is obviously impractical where a large number is in constant use.

In seeking to overcome such difficulties, it was found that certain types of glass beads can be ground to an exact diameter with a great deal of precision. However, different lots of glass beads vary widely in specific gravity and quite often beads in the same lot will vary, in part because of different compositions of the individual beads, and also because of the occlusion of small air bubbles. These conditions prompted the authors to select a "standard" sphere of closer specifications than that recommended by the Cellulose Division of the American Chemical Society and then to make all other beads have the same time of fall through standard castor oil. The selection of such a standard sphere and the method employed for matching this standard with other spheres are described below.

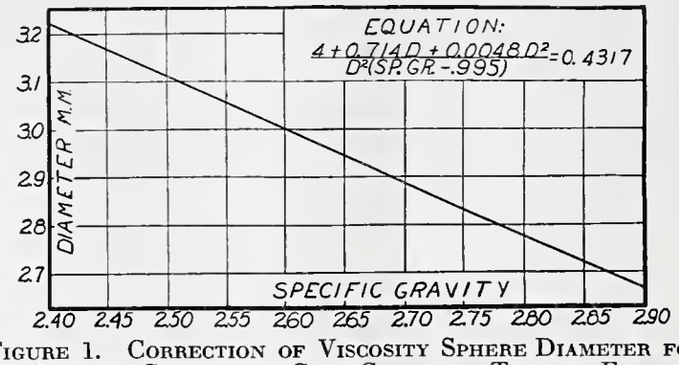

Figure 1. Correction of Viscosity Sphere Diameter for Specific Gravity to Give Constant Time of Fall

Selection of Standard Sphere

The American Chemical Society standard method calls for a glass sphere 0.125 inch (3.175 mm.) in diameter and having a specific gravity ranging between 2.4 and 2.6.

The beads on hand, when difficulties were encountered in obtaining additional supplies, had a diameter of 3.17 mm. and a specific gravity of 2.45. These spheres fell through standard castor oil of 686 centipoises at 25° C. in a standard viscometer tube (A. C. S.) at a rate equivalent to 22.3 centipoises per second of fall. Since these spheres are well within the A. C. S. limit they were set up as the standard for comparison of all future lots of beads.

Procedure for Calibration

The essential steps in obtaining spheres which will give the same time of fall as the standard sphere are as follows: selection from laboratory supply houses of glass beads approximately 4 mm. in diameter; segregation of these beads by means of dense liquids into batches having narrow limits of specific gravity; and grinding these beads on the basis of their average gravity to a diameter which has been determined from the Ladenburg modification of Stokes' law (*2*, *3*).

Selection of Beads. The selection of the unground beads is important because the Hartford Steel Ball Company, Hartford, Conn., has found that not all beads will stand

grinding. When grinding beads for the authors, the company states that regardless of diameter the beads should be of regular shape and free from "tips," surface chips, or other irregularities. It is also essential that the diameter be not greater than 4 mm., as otherwise too much grinding would be required for the ordinary specific gravities encountered in glasses.

Segregation of Beads. The segregation of any one lot of beads according to gravity is accomplished by the following steps:

1. Using 100 to 125 beads, determine the average specific gravity by weighing in a pycnometer.
2. Using the average specific gravity as the correct gravity, separate all the beads by placing them in a liquid of specific gravity 0.03 unit higher than the average gravity. All beads which float are removed from the liquid and washed. Those beads which settle out are too heavy and may be discarded altogether, or saved and further separated, depending on the amount of beads.
3. Those beads which floated (step 2) are placed in a liquid of specific gravity 0.03 unit lower than the average gravity of the beads. All beads which float in this mixture can be discarded, while those which sink are recovered and washed.

The two liquids which have been found to work very well are tetrabromoethane (sp. gr. 2.95) and tetrachloroethane (sp. gr. 1.588). For any gravity between 1.59 and 2.95 calculate the amount of each liquid to use and mix in these quantities. The specific gravity will come out very close to its calculated value but to be on the safe side, the gravity should be checked by pycnometer.

These liquids are good rubber solvents and should not be kept in rubber-stoppered flasks or used in equipment having rubber connections. The liquids are also volatile to a slight extent and should not be left exposed for great lengths of time. However, the gravity change while separating one batch of beads is not serious, as shown by the following figures:

Sp. Gr. at Start	Sp. Gr. after Being Used and Filtered
2.854	2.858
2.781	2.789

The use of beads within the range 0.06 unit in specific gravity is based on the error introduced in the final viscosity measurements. It can be shown through a consideration of Stokes' law that a 1 per cent variation in specific gravity at constant radius introduces a 1.35 per cent error in the final viscosity. The 0.06 limit allows a total error in viscosity of 3 per cent or only ±1.5 per cent.

A convenient arrangement for separating the beads after they have been placed in the liquid consists of a short piece of large-bore glass tubing, sealed off at one end. The other end of the tubing carries a side arm of sufficient diameter to allow the beads which float to pass through. A quantity of liquid of the required specific gravity is placed in the large tube and a few beads are added. These beads are agitated a few times with a glass rod and when those which will settle have settled, more liquid is carefully added until the beads which float pass out through the side arm. The beads and liquid can be separated by pouring through a Gooch crucible. The liquid thus separated can then be used over again. The liquid may become dirty while in use, but it is easily cleaned by filtering through filter paper.

The liquid which adheres to the beads may be easily removed by washing with either alcohol or ether.

Grinding to Proper Diameter. The proper diameter to which these beads are to be ground is calculated on the basis of the average specific gravity of the segregated beads. This is done by means of the Ladenburg modification of Stokes' law:

$$9\eta S(1 + 2.4\,x)(1 + 3.3\,r/h) = 2gr^2(d_1 - d_0)T$$

where η = viscosity of the liquid
S = distance fallen through in time T
r = radius of the sphere
d_1 = density of the sphere
d_0 = density of the liquid
g = acceleration due to gravity
h = height of liquid in the tube
x = ratio of the radius of the sphere to the radius of the tube

Grouping the terms which are independent of specific gravity and radius, and solving for T, we get

$$T = K\,\frac{(1 + 2.4\,x)(1 + 3.3\,r/h)}{r^2(d_1 - d_0)}$$

Since the intention is to prepare beads which all give the same time of fall (T), then the expression

$$\frac{(1 + 2.4\,x)(1 + 3.3\,r/h)}{r^2(d_1 - d_0)}$$

for the standard bead must be equivalent to the same expression for the unknown. On substituting the fixed constants of the standard sphere and the viscometer, the equation becomes

$$\frac{1 + 0.357\,r + 0.0048\,r^2}{r^2(\text{sp. gr. of bead} - \text{sp. gr. of solution})} = 0.4317$$

For cuprammonium solutions of cellulose as the authors prepare them the specific gravity of the solution is 0.995. On the basis of this gravity Figure 1 shows at once the diameter to which glass beads of any specific gravity must be ground in order to produce spheres equivalent to the standard in respect to time of fall.

The calculated diameter must be closely adhered to, for it can be shown from the above equation that a 1 per cent decrease in the radius of a sphere at constant specific gravity will increase the time of fall by 2.14 per cent. Results confirm these calculations.

Results

So far three lots of beads have been ground down to a calculated diameter. The data on these three lots are as follows:

Lot	Specific Gravity	Calculated Diameter	Actual Diameter	Centipoises per Second
		Mm.	*Mm.*	
Standard	2.45	...	3.17	22.3
1	2.77	2.81	2.795	22.4
2	2.81	2.77	2.82	23.2
3	2.74	2.845	2.84	22.33

It is seen that lot 2 fell 4 per cent too fast, the calculated diameter having been exceeded by 2 per cent. Other than this the results were very satisfactory, even though the diameter and gravity varied quite widely from the original specifications of the A. C. S. method.

Conclusions

It is possible and feasible to prepare, from beads having varying specific gravities, large quantities of beads all of which have the same time of fall through standard castor oil. Beads thus prepared will give just as accurate results as individually calibrated beads and after the selection of a standard bead, viscosity results may be reported in seconds or poises with equal accuracy.

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The Microanalysis of Gases

II. Carbon Monoxide, Ethylene, and Acetylene

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The method earlier described by the authors for the microanalysis of gases, using dry reagents, is here extended. The apparatus has been improved, and procedures have been devised for the determination of carbon monoxide with silver oxide, of ethylene with fuming sulfuric acid, and of acetylene with a mixture of cuprous chloride and potassium hydroxide.

In an earlier publication (*1*) an apparatus and method were described for the microanalysis of certain gases by means of solid reagents. Water vapor was removed by means of fused phosphorus pentoxide, carbon dioxide by fused potassium hydroxide, and oxygen by yellow phosphorus. Hydrogen, carbon monoxide, and methane were determined by means of the above reagents used in conjunction with an explosion process. The volumes of samples used were of the order of 0.1 cc.

In the present paper some improvements of the apparatus are described and new methods of analysis are given for carbon monoxide, ethylene, and acetylene. Results of analysis for these gases are included.

Improvements in Apparatus and Method

The number of inquiries which the authors have received in regard to this method of analysis has made it seem advisable to describe somewhat in detail certain portions of the apparatus and technic which have been employed. However, it is assumed that the original description (*1*) is available to the reader.

In Figure 1 are shown two important alterations of the apparatus which was previously described. Formerly, the gas sample and the mercury were moved up or down the microburet by applying pressure to a heavy-walled rubber tube. Although this method of manipulation is simple and can be used with satisfaction by the experienced operator, there is always a hysteresis effect in the rubber which causes annoyance. The device represented by *P*, *R*, *S*, and *B* in Figure 1 was worked out to overcome this effect. *P* is an iron cylinder into which the bell-shaped lower end of the buret is cemented by the sealing wax *N*. The wax is also used here to close the water jacket of the buret. *R* represents an elastic rubber cap. The lower flange of this cap is firmly secured against the lower edge of *P* in a manner which may be deduced from a study of the drawing. *S* is a metal plunger which is attached by a swivel to the screw *B*. The space above *R* is filled with mercury. By manipulating *B*, the plunger is forced either up or down, causing a flow of mercury or of gas through the capillary buret, *A*. In addition to overcoming the hysteresis effect, this arrangement gives a more positive and delicate control of the volume change in the system than was formerly obtained. It is designed to be dismantled and reassembled with ease, so that cleaning the buret is not a difficult task. Since *P* is the only one of the metal parts which comes in contact with the mercury, it is the only one which must be made of some nonamalgamating material.

The second improvement in the design of the apparatus consists of placing the absorbent holder guides *K* directly on the shaft which supports the gas holders *H* and *J*. Since in reality there are four absorbent holders symmetrically arranged around the shaft, this means that several separate analyses may be in progress at one time. A rubber band, made by cutting a short length from a suitable rubber tube, prevents the absorbent holder *L* from extending too far into the gas sample.

In Figure 1, *K* and *J* are shown projected on a vertical plane. Their relative positions are shown more clearly in Figure 2, in which the spider supporting the four guides is shown properly oriented above the one which supports the gas holders. The gas holders are held in position by steel ribbon springs.

The microburet which was first described was ruled arbitrarily in millimeter divisions, but is now graduated to read directly in cubic millimeters with the zero mark at the top of the scale.

One of the major difficulties encountered in this system of microanalysis arises from contamination of the open mercury surface. The gas holders and absorbents are put in place through this surface and if it is not clean, impurities will get on the inside walls of the holders and eventually into the capillary buret. To eliminate this it has been the authors' practice to apply suction immediately, through a capillary tube, to this surface whenever any scum or dust particles are discovered. It has been found much more simple to keep the surface clean by this constant vigilance than to allow it to become coated with an appreciable film before cleaning. A trap, of course, is placed in the suction line to catch the mercury which is drawn up with the impurities. Very little mercury will be removed from the reservoir in this way if the above procedure is followed and that which is removed may be returned from time to time, after it has been cleaned.

A number of clean gas holders (*H* and *J*, Figure 1) are ordinarily kept on hand and a new one is used for each analysis.

Specific Methods of Analysis

Carbon Monoxide. Especially prepared dry silver oxide has been found to be a very satisfactory selective absorbent for carbon monoxide. In the preparation, the oxide is precipitated by means of a strong base and thoroughly washed by decantation. While still somewhat moist, the solid is compressed into pellets by applying a pressure of approximately 6000 pounds per square inch. These pellets are allowed to dry at room temperature. Since they take up carbon dioxide, they must not be unduly exposed to the atmosphere.

The solid absorbents which have been described hitherto may be fused into the platinum loop of the holder. This procedure cannot be used for silver oxide since it decomposes at a comparatively low temperature. Hence, to introduce this substance into the gas sample the following expedient is used: Instead of a loop, a straight platinum wire is employed. The tip of this is moistened with a minute amount of a concentrated sodium silicate solution and then touched to a piece of the oxide. A regular shaped piece about 1.5 mm. in diameter

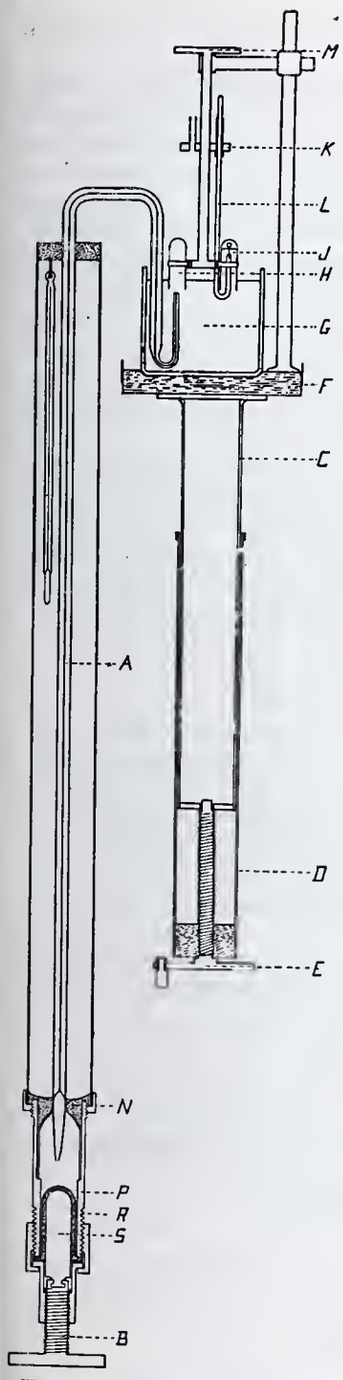

Figure 1. Diagram of Apparatus for Microgas Analysis

is to be preferred. Care is taken not to cover more of the surface of the oxide with the cement than is necessary to make it adhere. The cement is allowed to dry for 15 minutes, after which time there is no danger of losing the absorbent when it is being introduced into the gas holder. Furthermore, the drying reduces the vapor pressure of the cement to a negligible factor in the analysis. Absorption is usually complete in 10 minutes. No volatile products are formed in the reaction, so a follow-up absorbent is not required.

Table I gives results of several analyses for carbon monoxide in the presence of dry air, free from carbon dioxide. The volume of samples in all tables is given in cubic millimeters.

Ethylene. To the authors' knowledge, the selective absorption of the unsaturated hydrocarbons by means of a solid reagent has never been quantitatively successful. For reasons which have been given (*1*), it was not desired to resort to the use of liquid reagents after the procedure outlined by Christiansen (*2*). These objections have been overcome by using a porous sintered glass bead for introducing the liquid reagents. A piece of sintered glass is shaped to a sphere of approximately 2 mm. in diameter. This is attached to a straight platinum wire by heating the wire and letting the end of it become embedded in the bead. This process does not appreciably diminish the porosity of the bead. The use of this porous bead is illustrated in the following procedure for the absorption of ethylene.

Table I. Results of Analysis for Carbon Monoxide

Determination	Volume Sample	Carbon Monoxide Theoretical	Carbon Monoxide Determined	Difference
	Cu. mm.	%	%	%
1	80.27	49.69	49.62	−0.07
2	72.04	49.69	49.61	−0.08
3	66.09	49.69	49.57	−0.12
4	58.95	49.69	49.16	−0.08
		Average difference		−0.09
		Average deviation from mean		0.02

In analyzing for ethylene, the bead is dipped slowly into fuming sulfuric acid. The space in the bead becomes filled with the liquid and the air is forced out. The bead is wiped with a piece of filter paper to remove the excess acid from the exterior surface and then introduced in the usual way into the gas sample. Almost instantaneous absorption occurs. After 2 minutes the acid is removed and a slightly moist potassium hydroxide bead is added to take up the sulfur trioxide vapor. This absorption is also very rapid. After another 2 minutes the solid may be removed and the decrease in volume of the sample, due to the presence of unsaturated hydrocarbons, is measured.

Table II gives results of analyses by this method of mixtures of ethylene and butane for ethylene. In these cases a new sample was prepared for each determination, hence the different theoretical percentages of ethylene.

Table II. Results of Analyses of Ethylene and Butane Mixtures

Determination	Volume Sample	Ethylene Theoretical	Ethylene Determined	Difference
	Cu. mm.	%	%	%
1	137.53	50.04	50.04	0.00
2	141.89	51.81	51.83	+0.02
3	132.89	50.53	50.53	0.00
4	58.88	51.27	51.21	−0.06
5	125.63	50.15	50.26	+0.11
		Average difference		+0.04
		Average deviation from mean		0.04

Acetylene. In order to remove acetylene quantitatively from mixtures with hydrocarbons of the ethylene and methane series, an attempt was made to use a sintered glass bead filled with an ammoniacal solution of cuprous chloride, following this with moist phosphorus pentoxide to remove the ammonia. Absorption occurred, but sufficient reagent could not be introduced in a single bead to remove all of the acetylene present in the average sample. However, the principal disadvantage of the method was the collection of a voluminous precipitate of copper acetylide on the exterior of the bead, which contaminated the mercury surface as the bead was being removed.

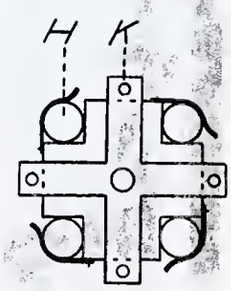

Figure 2. Diagram Showing Relative Positions of Gas Holders and Absorbent Holder Guides

Solid cuprous chloride, when moistened, will absorb some acetylene, but the reaction does not go to completion unless a base is used in conjunction with the chloride in order to remove the hydrogen chloride produced. It was found that this principle can be used in the following manner for the analysis for acetylene, without the objections arising from the use of a solution.

A stiff paste is made by moistening cuprous chloride with a dilute potassium hydroxide solution. This is molded in the platinum loop of an absorbent holder and heated gently until dry, care being taken not to heat the solid until it turns dark in color. This bead gives complete absorption of the acetylene contained in the average sample in less than 5 minutes. The copper acetylide formed in the reaction becomes an integral part of the solid bead and does not contaminate the mercury as it is being removed from the reaction system. The potassium hydroxide takes up all of the hydrogen chloride or water vapor formed in the process, so that the decrease in volume gives directly the amount of acetylene which is present. Mixtures of acetylene with butane and with ethylene have been analyzed by this method with the success shown in Tables III and IV.

Table III. Results of Analyses of Acetylene and Butane Mixtures

Determination	Volume Sample	Acetylene Theoretical	Acetylene Determined	Difference
	Cu. mm.	%	%	%
1	137.53	45.20	45.00	−0.20
2	137.42	45.33	45.33	0.00
3	136.92	45.13	45.03	−0.10
4	136.89	45.14	45.18	+0.04
5	136.97	45.14	45.10	−0.04
		Average difference		−0.08
		Average deviation from mean		0.06

Table IV. Results of Analyses of Acetylene and Ethylene Mixtures

Determination	Volume Sample	Acetylene Theoretical	Acetylene Determined	Difference
	Cu. mm.	%	%	%
1	137.97	45.98	45.73	−0.25
2	129.80	49.25	49.33	+0.08
3	136.75	41.96	42.06	+0.10
4	136.10	45.35	45.35	0.00
5	135.76	44.82	44.62	−0.20
		Average difference		0.13
		Average deviation from mean		0.14

Discussion of Results

The use of silver oxide as an absorbent was suggested by the work of Lamb and his associates (*4*, *5*, *6*) on the catalytic oxidation of carbon monoxide by the hopcalites. In the microanalysis of gases, where the expense of reagents is a negligible factor, silver oxide is superior to the hopcalites not only because it reacts more rapidly, but also because any carbon dioxide which may be produced is immediately absorbed by more silver oxide. According to Gautier (*3*), the reaction for the absorption of carbon monoxide may be represented as:

Figure 3. Micro-gas Analysis Apparatus

Complete except mercury and absorbent holders.

$$2Ag_2O + CO = 2Ag + Ag_2CO_3$$

The authors' experience substantiates this, since free silver is produced in the process and no carbon dioxide is liberated. The decrease in volume represents the volume of carbon monoxide present in the sample.

The presence of hydrogen introduces an appreciable error in the determination of carbon monoxide by this method. However, the rate of absorption of hydrogen by dry silver oxide is so slow compared to the rate of carbon monoxide absorption that the method can be used in many cases, providing the time of exposure is properly regulated. In a series of experiments (*7*) it was found that in an average analysis of a sample containing equal quantities of carbon monoxide and hydrogen an error of approximately 1.25 per cent in the carbon monoxide may be expected. The magnitude of this error depends (*a*) upon the physical state of the silver oxide, (*b*) upon the amount of hydrogen and nonreacting gases present, and (*c*) upon the time of exposure. It is important that the silver oxide be dry in order to minimize the hydrogen oxidation. For the purpose for which it was developed, the authors have found this method of separation of these two gases to be satisfactory. However, in the hope of making further improvements the problem is being given additional consideration.

The method given here for the analysis of ethylene is generally applicable to the analysis of unsaturated hydrocarbons in the presence of hydrogen, the methane series, and the other more inert gases. In cases in which fuming sulfuric acid is not needed for the absorption, the treatment with potassium hydroxide is omitted. Since the acid remains in the bead and does not contaminate the mercury surface in the gas holder, there is no danger of getting the reagent and impurities in the buret. The very small amount of liquid reagent used reduces to a minimum the possible errors due to the dissolving of the remaining gases.

The sintered glass may be made in any laboratory by taking ground glass of the proper mesh and heating it carefully until the pieces just begin to fuse. This use of a sintered bead opens up the possibility of using any of the liquid reagents of macroanalysis for the microanalysis of gases. At the same time it eliminates the usual objections to liquids. However, experimental difficulties, such as those encountered in analyzing for acetylene with an ammoniacal cuprous chloride solution, may prevent the use of certain solutions. Most water solutions used in this way would require a follow-up bead to take out water vapor, for it has been found (*1*) that the normal vapor pressure of water cannot be assumed to exist in these reacting systems.

It is felt that the results given in the accompanying tables are typical of those which may be expected from the methods which are given. In following the course of certain photochemical reactions, over two hundred determinations of carbon monoxide by the silver oxide method have been made in the authors' laboratories with most satisfactory results.

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Chain Arrangement for Rubber Stoppers

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Glass stoppers are easily attached to the necks of their containers by means of a cord or chain. This practice prevents loss, exchange, or contamination of the stopper. No satisfactory means of fastening a rubber stopper to a container (for alkali or other solutions) has come to the authors' attention.

A method for doing this follows: Place a stopper (of any suitable size) in a lathe and drill through the top end into the center with a 0.06-inch (0.16-cm.) centering drill, followed by a 0.187-inch (0.48-cm.) drill. Insert a 0.187-inch recessing tool to the center of the stopper, where a hole 0.125 inch (0.32 cm.) wide and 0.31 inch (0.8 cm.) in diameter is made. Select a piece of brass rod of 0.31-inch (0.8-cm.) diameter and of suitable length and machine to the size and shape of the hole in the stopper. Round off the lower edges of this plug, drill a 0.06-inch (0.16-cm.) hole in the upper end of the shaft for the purpose of attaching a chain, and insert in the stopper using glycerol, rubber cement, or water as a lubricant.

The time required for the complete operation is less than 5 minutes.

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Volumetric Determination of Cobalt by Means of Ferrous Sulfate and Potassium Dichromate

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ENGLE and Gustavson (*2*), Willard and Hall (*5*), and others (*3*) have shown that cobalt can be determined easily and accurately by precipitating it as cobaltic hydroxide with sodium hydroxide in the presence of sodium perborate, decomposing the excess of the latter by boiling, dissolving the suspended precipitate by the addition of an acidified solution of potassium iodide, stannous chloride, or titanous sulfate, and finally titrating the liberated iodine, or excess of reducing agent by standard methods.

However, the iodometric method is unsatisfactory in the presence of even a small amount of ferric iron, and requires from 0.5 to 2 hours for dissolving the precipitate, while stannous and titanous solutions require special handling because of their great sensitivity to atmospheric oxidation. Willard and Hall (*5*) attempted to use a strongly acid solution of ferrous sulfate as reducing agent, but obtained results which were consistently more than 4 per cent too low. On the other hand, the natural advantages of ferrous sulfate and potassium dichromate as titrating solutions have been recently increased by the discovery of the sensitive and reliable internal indicator diphenylamine sulfonic acid (*4*), and it has seemed desirable to develop a satisfactory procedure for their use in the determination of cobalt.

It is probable that the low results of Willard and Hall were due to the great instability of cobaltic salts in acid solution, and that some free oxygen was lost while mixing with the strongly acid ferrous sulfate, since the latter is comparatively resistant to the action of oxygen in the cold. Such a possibility gave rise to the hope that an accurate procedure could be developed for the use of ferrous sulfate in the titration of cobalt, and has led to this research.

SOLUTIONS

The cobalt solution was made up from pure anhydrous cobalt sulfate, and proved to be free from nickel by testing with dimethylglyoxime; the mean of six electrolytic depositions (*1*) showed a cobalt content of 0.0495 gram (0.0495, 0.0494, 0.0495, 0.0495, 0.0496, and 0.0495 gram) for each 25-cc. portion at 25° C.

The titrating solutions were 0.1 *N*, but much weaker ones could be employed if desired. The potassium dichromate was made up to a definite volume with water from an accurately weighed portion of the pure recrystallized salt. The solution of pure ferrous ammonium sulfate, slightly acid with sulfuric acid, was standardized frequently against the dichromate in the presence of phosphoric acid, using 5 drops of a 0.2 per cent water solution of barium diphenylamine sulfonate as indicator.

MANNER OF MIXING REAGENTS

EFFECT UPON FERROUS IRON. It is necessary in this analysis to mix an acidified ferrous sulfate solution with a considerable quantity of sodium hydroxide, without change of titer; otherwise, apparently correct results for cobalt would be due to a compensation of errors. Many experiments were made with the greatest care, allowing each solution to flow down the walls of the flask underneath the other reagents, but some iron was always oxidized when air was present. A layer of ether prevented this fairly well when the ferrous solution was added to the base, but not when the order was reversed. The titer was unchanged, however, when the mixing was done in an oxygen-free atmosphere, regardless of the temperatures or the order of addition of the reagents.

EFFECT UPON TITRATION OF COBALT. Low results were always obtained when the strongly alkaline solution containing precipitated cobaltic hydroxide was mixed with ferrous iron in the presence of enough sulfuric acid to neutralize all the base, regardless of the temperature or manner of mixing; naturally, the titration value of the iron was determined under parallel conditions in each case. The values were still lower when the mixing was performed under a layer of ether, and not even working in a completely closed air-free vessel sufficed to correct the error. However, when ordinary weakly acid ferrous sulfate solution was added to the alkaline mixture in an air-free flask, with subsequent acidification by sulfuric acid, the results were quantitative, even at the boiling temperature. A 500-cc. Erlenmeyer flask fitted with a dropping funnel of 35 to 40 cc. capacity by means of a well-paraffined rubber stopper can be used for this purpose, but it is difficult to prevent the leakage of a little air, to which ferrous hydroxide is very sensitive; an all-Pyrex apparatus with ground-in dropping funnel is preferable.

RECOMMENDED PROCEDURE

The cobalt solution, free from interfering ions and containing at least 5 cc. of 6 *N* sulfuric acid and 1 to 2 grams of dissolved sodium perborate, is treated with enough 6 *N* sodium hydroxide to leave about 10 cc. in excess, whereupon brownish black cobaltic hydroxide precipitates, accompanied by active effervescence; the mixture is boiled for 10 minutes to decompose excess of perborate and displace last traces of oxygen by water vapor, the dropping funnel being placed in position (with the stopcock open) and paraffined near the end of this period. After removal from the hot plate the apparatus is promptly closed and an excess of standard ferrous sulfate measured into the funnel; upon opening the stopcock cautiously, the solution is drawn in by the reduced pressure inside the flask, taking care that no air is allowed to enter. The funnel is rinsed with two or three portions of water, always avoiding the entrance of air, the vessel is shaken a few seconds, and 25 to 30 cc. of 6 *N* sulfuric acid are admitted, whereupon the precipitate dissolves almost instantly. After cooling to room temperature, the stopcock is opened, and the funnel removed and rinsed. About 10 cc. of 25 per cent phosphoric acid and 5 drops of a 0.2 per cent water solution of barium diphenylamine sulfonate are then added, and the excess of ferrous iron titrated to the appearance of a violet with standard dichromate. The method thus becomes extremely rapid.

INTERFERING IONS. Nitrates and other oxidizing substances which give colorations with diphenylamine sulfonic acid must be absent. Nickel does not interfere. Cobalt can be easily separated in one operation from manganese, chromium, vanadium, etc., by means of phenylthiohydantoic acid (*5*); small amounts of iron are carried down with this precipitate, but not enough to cause incomplete oxidation of the cobalt by perborate.

Table I. Determination of Cobalt

Experiment	0.1 N $K_2Cr_2O_7$ Used Analysis	Blank	Cobalt Present	Found	Error
	Cc.	Cc.	Gram	Gram	%
1	15.89	24.28	0.0495	0.0495	0.0
2	15.87	24.28	0.0495	0.0496	0.2
3	15.88	24.28	0.0495	0.0495	0.0
4	15.91	24.28	0.0495	0.0494 −	−0.3
5	15.91	24.28	0.0495	0.0494 −	−0.3
6[a]	16.28	24.70	0.0495	0.0496 +	0.3
7[a]	16.32	24.70	0.0495	0.0494	−0.2
8	16.34	24.77	0.0495	0.0497	0.4
9	16.37	24.77	0.0495	0.0495	0.0
10	16.41	24.77	0.0495	0.0493	−0.4
11	16.40	24.77	0.0495	0.0494 −	−0.3
12	16.40	24.77	0.0495	0.0494 −	−0.2
13	16.35	24.77	0.0495	0.0496 +	0.3
14	16.37	24.77	0.0495	0.0495	0.0
15	16.33	24.77	0.0495	0.0497 +	0.5
16	16.34	24.77	0.0495	0.0497	0.5
17	16.32	24.77	0.0495	0.0498	0.6
18	16.37	24.77	0.0495	0.0495	0.0
19	8.02	24.77	0.0990	0.0988	−0.2
20	8.00	24.77	0.0990	0.0989	−0.1

[a] Experiments 6 and 7 contained 20 and 40 mg. of nickel, respectively.

Accuracy. A few typical results are given in Table I to illustrate the accuracy which is possible by this method. Experiments 1 to 5 were performed in an apparatus constructed entirely of Pyrex, while 6 to 20 were carried out in an ordinary apparatus with a paraffined rubber stopper.

Summary

The method described above has been developed for the use of sodium perborate, ferrous sulfate, and potassium dichromate in the volumetric determination of cobalt, and is believed to be the most rapid, convenient, and accurate so far proposed. Diphenylamine sulfonic acid is recommended as indicator.

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Nomograph for Rapid Calculation of Sulfate-Carbonate Ratios

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A LARGE number of plants and laboratories calculate ratios of sodium sulfate to total alkalinity when expressed as sodium carbonate, to ascertain whether or not the result is within the limits as prescribed by the American Society of Mechanical Engineers for the inhibition of caustic metal embrittlement. Most laboratories report sulfates in terms of the radical SO_4 and alkalinities in terms of calcium carbonate. To convert sulfates to sodium sulfate, it is necessary to multiply by 1.479—that is, $SO_4 \times 1.479 = Na_2SO_4$. To calculate total alkalinity as calcium carbonate in terms of sodium carbonate, it is necessary to multiply by the factor 1.06—that is, $CaCO_3 \times 1.06 = Na_2CO_3$. To calculate the sulfate-carbonate ratio, the first result is divided by the second.

The accompanying nomograph accomplishes the same result in one operation. Given sulfates in terms of SO_4 and total alkalinity in terms of $CaCO_3$, the ratio $\frac{Na_2SO_4}{Na_2CO_3}$ may be read by extending a straight line from the total alkalinity axis at the given figure through the given figure on the sulfate axis and reading the result directly on the ratio axis.

A. S. M. E. Requirements. The ratio in each case is the minimum ratio required.

For pressures up to 150 pounds, 1 part sodium sulfate to 1 part total alkalinity.

For pressures from 150 to 250 pounds, 2 parts sodium sulfate to 1 part total alkalinity.

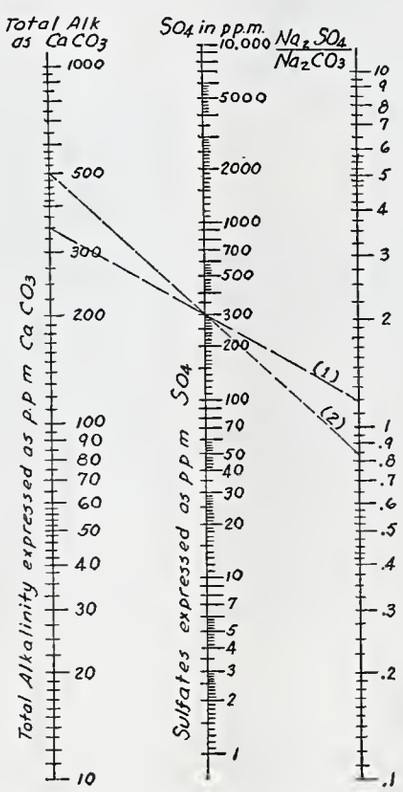

Figure 1. Nomograph for Calculating Sulfate-Carbonate Ratios for Inhibition of Caustic Metal Embrittlement

For pressures over 250 pounds, 3 parts sodium sulfate to 1 part total alkalinity.

The following examples illustrate the use of the chart:

Example 1. Given an analysis in parts per million, part of which reads as follows:

Sulfates (SO_4)	300
Alkalinity as $CaCO_3$:	
Bicarbonates	0
Carbonates	154
Hydroxides	196

The total alkalinity, the sum of carbonates and hydroxides as given in this analysis, is 350 parts per million. Start a straight line from this point on the total alkalinity axis intersecting the sulfate axis at 300 parts per million and the corresponding ratio will be found to be 1.19 on the ratio axis. This ratio is satisfactory for boilers operating below 150 pounds pressure but is unsatisfactory for boilers over 150 pounds. Mathematically, the following calculations would have been required:

$$\frac{SO_4 \times 1.479}{CaCO_3 \times 1.06} = \frac{300 \times 1.479}{350 \times 1.06} = 1.19$$

Example 2. Given an analysis in parts per million, part of which reads as follows:

Sulfates (SO_4)	300
Alkalinity as $CaCO_3$:	
Bicarbonates	0
Carbonates	188
Hydroxides	312

The total alkalinity, the sum of carbonates and hydroxides as given in this analysis, is 500 parts per million. Start a line from 500 parts per million on the total alkalinity axis, intersecting the sulfate axis at 300 parts per million, and it will strike

the ratio axis at 0.84. This ratio is unsatisfactory for boilers operating at any pressure.

The chart may also be used by those working with results in terms of grains per U. S. gallon without converting to parts per million, because the conversion factor from parts per million to grains per gallon is cancelled in the ratio. To aid in reading, however, the figures on both the total alkalinity and the sulfate scales should be divided by 10. For example, if sulfates were given as 30 grains per gallon (Example 2), and total alkalinity as 50 grains, the resulting ratio would be 0.84.

ACKNOWLEDGMENT

The author wishes to acknowledge the kind assistance of E. M. Ross for his help in certain calculations and preparations of the nomograph.

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Identification of Amines as 3,5-Dinitrobenzoates

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THE amine salts of various sulfonic acids (*2*, *5*) have been recommended as derivatives for the identification of amines. This investigation concerns itself with the carboxylic acid—3,5-dinitrobenzoic acid—which appears to offer some advantages over the sulfonic acids as a reagent to be used in amine identification. In brief, it may be stated that the 3,5-dinitrobenzoic acid is more readily available or more easily prepared; it combines with a great variety of aliphatic and aromatic amines to form salts which usually have low, sharp melting points; and the salts, as a rule, are easily prepared and purified.

Although the amine salts of 3,5-dinitrobenzoic acid are not as stable as the acetyl or benzoyl derivatives of the amines, their stability is such that recrystallization commonly leads to compounds having melting points sufficiently definite for identification purposes. Frequently the former are more easily prepared in a pure state than the latter. In addition, while the acyl derivatives may be formed with primary and secondary amines, the 3,5-dinitrobenzoates are capable of being produced for all types of amines. Failures in the latter case appear to be due to the insufficient basicity of the amine.

The results are summarized in Table I, which also contains for comparison the melting points of the corresponding *p*-toluene sulfonates. None of these compounds, with the exception of those of ammonia (*3*) and pyridine (*7*), appear to have been described.

TABLE I. 3,5-DINITROBENZOATES OF AMINES

Amine	Recrystallizations	Melting Point Obs. °C.	Melting Point Corr. °C.	Color	Molar Ratio	Neutral Equivalent Calcd.	Neutral Equivalent Found	Nitrogen Calcd.	Nitrogen Found	Melting Point (*5*) of *p*-Toluene Sulfonate
Aniline	1	132.8	134.7	Light yellow	1:1	305.1	302.7	13.77	13.65	238.4
o-Toluidine	1	132.8	134.9	White	1:1	319.1	313.8	13.17	13.13	189.7–190.5
m-Toluidine	0[a]	137.0–142.0	139.0–144.0	Light yellow	1:1	319.1	317.5	13.17	13.20	174.6–176.1
p-Toluidine	1	142.6–145.0	145.0–147.4	Orange	1:1	319.1	316.3	13.17	13.14	197.7–199.2
4-Amino-1,3-dimethylbenzene	2	166.0–166.8	169.6–170.4	Light tan	1:1	333.1	339.0	12.61	12.52	180.4–181.3
o-Chloroaniline	1	150.2	152.7	Bright yellow	1:1	339.6	341.9	12.38	12.28	192.9–193.6
m-Chloroaniline	1	120.3	121.8	Yellow	1:1	339.6	339.1	12.38	12.37	209.8–210.3
p-Chloroaniline	1	131.4	133.0	Yellow	1:1	339.6	333.4	12.38	12.57	213–231
p-Bromoaniline	1	125.0	126.9	Yellow	1:1	384.0	381.2	10.94	10.94	214.2–234.2
o-Nitroaniline		No compound isolated								Oil
m-Nitroaniline	2[b]	110.6–113.0	112.0–114.4	Orange	1:1	350.1	341.9	16.00	16.12	213.5–215.0
p-Nitroaniline	1[b]	126.6	128.6	Yellow	1:1	350.1	342.6	16.00	16.09	232.2–234.7
p-Aminophenol	2	175.8–176.4	178.2–178.8	Yellow	1:1		[c]	13.09	12.88	252.1–253.6
o-Aminobenzoic acid	1	200.4–200.8	205.2–205.6[d]	Bright yellow	1:1	174.6	169.5	12.04	11.87	224.1–224.6
m-Aminobenzoic acid	1	164.0–169.2	167.0–172.2	Orange	1:1	174.6	176.9	12.04	12.01	255.9–256.5
p-Aminobenzoic acid	2	192.0	196.7	Orange	1:1	174.6	176.1	12.04	11.97	236.5–241.5
Methylaniline	0[a]	120.2	121.8	Light yellow	1:1	319.1	315.0	13.17	13.12	Oil
Dimethylaniline	1	113.2–114.0	114.8–115.6	White	2:1	272.6	272.1	12.85	12.66	Oil
Benzylaniline	2[e]	131.0	133.0[d]	Faint yellow	1:1	395.2	389.9	10.63	10.71	148.3–148.8
Dibenzylaniline		No compound isolated								Oil
Acetanilide	1	127.0–128.0	129.1–130.1	Yellow	1:1	347.1	339.9	12.11	12.00	.....
Diphenylamine		No pure compound isolated								.....
Triphenylamine		No compound isolated								.....
o-Phenylenediamine	1[e]	174.0	177.3[d]	Yellow	1:1	320.1	320.0	17.50	17.70	267.3–268.8
m-Phenylenediamine	0	155.8	158.7	Yellow	1:1	320.1	320.0	17.50	17.35	296.8–297.8
p-Phenylenediamine	2[e]	174.1–174.8	177.3–178.0[d]	Yellow	1:1	320.1	320.0	17.50	17.65	>340
α-Naphthylamine	2	195.8	200.5	Red	1:1	355.1	355.6	11.83	11.82	248.4–249.9
β-Naphthylamine	1	153.5–154.2	156.5–157.2	Yellow	1:1	355.1	348.2	11.83	11.74	217.3–219.1
Benzidine	1	200.6	205.7[d]	Light yellow	2:1	304.1	303.2	13.82	13.65	.....
Pyridine	1	168.2	171.3	Light yellow	2:1	251.6	249.6		[f]	Oil
Quinoline	1[g]	149.0–149.8	151.4–152.2	White	1:1	341.1	338.0		[f]	Oil
Ammonia	0	242.0	246.7	Yellow	1:1	229.1	231.2	18.34	18.40	.....
Benzylamine	1	205.0	210.0	Yellow	1:1	319.1	330.6	13.17	13.12	184.5–185.5
Diethylamine	2	161.2	163.4	Light yellow	1:1	285.1	286.8	14.74	14.60	.....
Triethylamine	0[a]	135.0–147.0	138.0–150.0	Light yellow	1:1	313.2	310.1	13.42	13.30	.....
Urea	2[e]	118.9	120.5	Light yellow	1:1	272.2	272.1	20.59	20.68	.....
Acetamide	0[a]	93.0–103.0	93.9–103.9	Light yellow	2:1	241.6	246.6	14.49	14.50	.....
Benzamide	2	136.4–138.2	138.6–140.4	White	1:1	333.1	325.2	12.62	12.73	.....

[a] Decomposition occurred on redissolving compound.
[b] Recrystallized from cold benzene.
[c] Determination was not possible because of intense color produced in solution.
[d] Compound turned dark below melting point.
[e] Recrystallized from mixture of alcohol and benzene.
[f] Nitrogen could not be determined by Kjeldahl method.
[g] Recrystallized from hot benzene.

Experimental

In general, to form the salts, 0.01 mole of each component was dissolved, by heating if necessary, in 25 to 50 cc. of absolute alcohol, after which the two solutions were poured together on a watch glass to crystallize. Purification was accomplished, unless otherwise stated in Table I, by recrystallization from absolute alcohol. The number of recrystallizations necessary for purity in each case is indicated in the second column of the table.

The melting points on the completely air-dried salts were determined by the method of Mulliken (*4*). A thermometer calibrated by the Bureau of Standards was employed and stem corrections were applied in all cases to obtain the corrected melting points.

The neutral equivalents were determined by the method of Perkin and Sewell (*6*) which, for the salts of aliphatic amines, was modified in that the titration was continued until the end point with phenolphthalein remained after boiling for 5 minutes. For the nitrogen analyses, the modified Kjeldahl method (*1*) was used.

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Amplified Ballistic Method for Measurement of Glass Electrode Electromotive Force

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The null instruments which have been used for balancing the voltage of a glass electrode system against the varied potential from a potentiometer are the vacuum tube voltmeter, the quadrant electrometer, and the recently suggested ballistic method of Morton (*4*). In the usual vacuum tube voltmeter method it is necessary to use a vacuum tube with a high grid resistance (*1*) which necessitates the use of a special vacuum tube (*2*, *3*, *5*). Because of the required shielding, the use of a quadrant electrometer is unsatisfactory. The authors have developed a circuit using the ballistic method, which has the advantages of the use of inexpensive vacuum tubes and elimination of electrostatic shielding, and will give the voltage of a glass electrode system in less than one minute to an accuracy of less than 0.5 millivolt. A vacuum tube amplifier is used to amplify the ballistic throw which makes it possible to use a less sensitive galvanometer. The apparatus used is routine laboratory apparatus and the circuit is easily assembled.

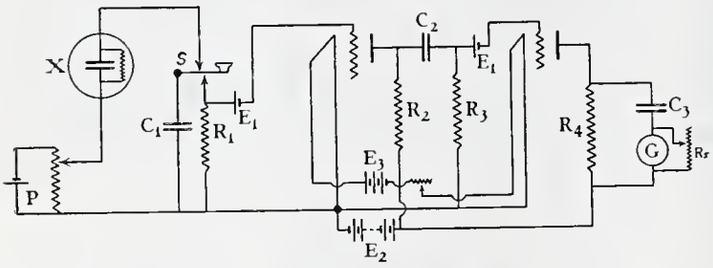

Figure 1. Diagram of Circuit

S, Leeds and Northrup single-contact short-circuit key
C_1, 0.1 μ farad (paper condenser)
C_2, 4 μ farads (paper condenser)
C_3, 2 μ farads (paper condenser)
R_1, 0.1 megohm
R_2, 0.5 megohm
R_3, 0.25 megohm
R_4, 10,000 ohms
R_5, variable galvanometer resistance

The circuit diagram is given in Figure 1. The condenser C_1 is charged to a potential equal to the difference of potential between the potentiometer P and the glass electrode system X. On tapping the key the condenser is discharged through the resistance R_1, the discharge being amplified by the vacuum tube circuit and indicated by the galvanometer G. When the voltage of the potentiometer is equal and opposite to that of the glass electrode assembly, the ballistic throw is zero. The vacuum tubes used are either UX240 or UX222. The galvanometer is a Leeds and Northrup moving coil instrument, either a shunted type R having a sensitivity of 0.003 amperes per mm. deflection or the enclosed lamp and scale type with a sensitivity of 0.025 amperes per mm.

By using a low grid resistance R_1 it is possible to eliminate shielding and at the same time avoid the use of an extra condenser in the discharging circuit, as recommended by Morton (*4*). It is necessary to use a by-pass condenser of a high capacity at C_2; otherwise the ballistic throw becomes of a complex oscillating nature, making adjustment difficult. The condenser on standing acquires a charge from the paper dielectric, the so-called absorbed charge; hence it is necessary to neglect the first throw, if the condenser has stood for some time without being discharged.

The use of a single stage of amplification resulted in increasing the throw six times. On introducing the second stage the ballistic throw was increased sixty times. A very satisfactory glass membrane is a bulb, 1 to 2 cm. in diameter, blown on the end of a tube of Corning H 015 glass of 5 mm. diameter. The inside of the bulb is filled with hydrochloric acid–potassium chloride buffer saturated with quinhydrone, and contact is made with this solution by means of bare platinum wire. Such an electrode maintains its calibration over a long period.

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The T-50 Test for State of Cure

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In tires, machine supports, conveyor belts, hose, waterproof clothing and footwear, and other rubber articles, the state of vulcanization of the rubber in the rubber compound is important for best results in service. A simple, rapid, and accurate physical test for state of cure is described, which is independent of the composition of the rubber compound. The test depends upon the observation that for a specific rubber compound the greater the state of cure the lower is the temperature at which chilled stretched rubber will spontaneously retract.

THE state of vulcanization or cure of rubber is one of the most important characteristics of vulcanized rubber. The expressions "undercure," "proper cure," "optimum cure," "overcure," and "reversion" are indicative of the qualitative nature of ideas on state of cure. According to Whitby (*7*), "the term 'state of cure' is intended to indicate the position of a cure in a series of progressive cures."

The physical properties of a vulcanized rubber compound should be differentiated from the state of cure. Thus, rubber compounds suitable for tire treads, tire carcass, footwear, clothing, artificial leather, or elastic webbing are all compounded or constructed so as to bring out to the fullest extent the physical properties which are best suited to their intended use. For each of these compounds there is a state of cure which will be most satisfactory. A simple, rapid, and accurate method for measuring the state of cure would be useful, and it is the purpose of this paper to describe such a test.

Historical

Four properties have been used to determine the state of cure: combined sulfur, or free sulfur in compounds of known total sulfur; optimum cure as exemplified by maximum tensile strength, maximum stress for a given strain, or tensile product; optimum resistance to deterioration or aging; and extent of indifference to heat and cold.

It was early recognized that the amount of combined sulfur was an important criterion of state of cure. About 1843, Hancock (*3*) dipped raw rubber strips in molten sulfur and observed that "it was now demonstrated that sulfur and sulfur alone, blended with the rubber, and acted on by heat at a proper temperature and for a relative period of exposure to its influence, was the sole cause for the change in the substance."

As tensile-testing equipment came into use it was gradually realized that a tensile property of a single sample of rubber was of itself practically valueless in determining the state of cure, for this property depends not only on the cure but also on the quality of the rubber and the type of compound, which in turn depends upon the kind and amount of accelerator, activator of acceleration, and nonrubber additions. It became customary to make a series of cures for a given rubber compound and ascertain by tensile testing the particular vulcanizate which possessed the optimum enhancement of this property (*7*). This was called the "optimum cure." As artificial aging tests began to be accepted it was found that the rubber cured at this so-called "optimum" as determined by tensile tests did not always resist aging as well as rubber at some other state of cure, which was called by some the "best cure."

Goodyear (*2*) states in his patent that rubber when vulcanized is "so far altered in its qualities as not to become softened by the action of the solar ray or of artificial heat—nor will it be injuriously affected by exposure to cold." From the beginning it has been recognized that vulcanization conferred on rubber a tremendous change in its resistance to softening at high temperatures and hardening at low temperatures, but very little practical use has been made of this knowledge in the routine testing of rubber for state of cure.

It was observed that a well-vulcanized piece of rubber, after having been chilled in the stretched condition in contact with ice, instantly retracts on being released. Unvulcanized or undercured rubber does not snap back, but slowly returns as it is warmed. This test was so rapid and useful that for several years it was called the "ice test." Unfortunately, the range and precision of the ice test are limited; the state of cure of many compounds is beyond the range of the ice test and pieces of frozen substances which melt below the melting point of ice are not readily available. The commercial production of solid carbon dioxide, however, has made it practical to evolve the present test.

The T-50 Test

The first step in the T-50 test consists of stretching a piece of rubber, chilling it to a low temperature while stretched, and releasing it. The rubber remains elongated, or, in other words, it is "racked." The next step consists of gradually heating the rubber and observing the temperature, T-50, at which the rubber has retracted to such an extent that it has lost 50 per cent of its original elongation. In many compounds, most of the retraction occurs in a fairly small temperature range, and the rate of contraction with increased temperature is usually greatest when the rubber has lost 50 per cent of its elongation.

The T-50 value for raw rubber is approximately +18° C. and it decreases as the extent of cure increases. It decreases also with time of cure, and with extent of combined sulfur. The T-50 test in many cases gives good correlation with combined sulfur computed on the basis of rubber content of the compound. Roughly, every decrease of 13° C. of the T-50 value represents an increase of 1 per cent of combined sulfur. There are sometimes large deviations from this correlation—for example, compounds containing reclaim, reverted cures, and some cases where ultra-accelerators are used, especially low-temperature cures—but this does not detract from the empirical use of the test. The test is particularly useful for these compounds after it has been standardized with a range of cures for the specific compound, since only one test piece or determination is required.

Racked Unvulcanized Rubber

When unvulcanized smoked sheet is stretched in hot water it can be drawn out to a thread. If this thread is cooled in the air and released, it remains elongated (*1*). In this condition the rubber is not elastic, but is more like catgut

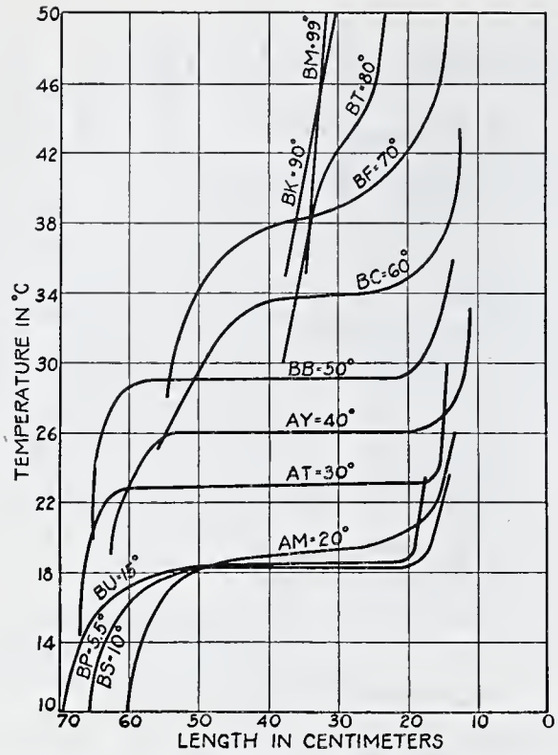

FIGURE 1. RETRACTION CURVES FOR RACKED RUBBER

than rubber, and is said to be racked. When this racked rubber is warmed it retracts and again becomes elastic. This phenomenon was investigated at different temperatures of stretching. The results are of interest in that the T-50 value of raw rubber was obtained from them and also in that the relation of this T-50 value to high-temperature racking is shown.[1] Figure 1 gives heating curves of rubber which had been racked at different temperatures. The racking temperatures are shown on each curve. The rubber retracts slowly with temperature at first and then very rapidly as shown by the plateaus of the curves. Finally, on further heating, a residuum of retraction occurs. From these curves it is seen that the retraction takes place at a

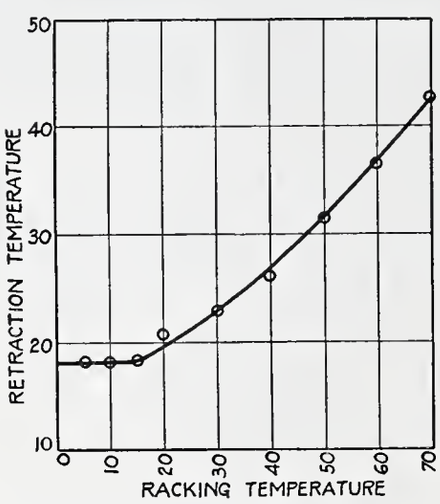

FIGURE 2. RETRACTION TEMPERATURE *vs.* RACKING TEMPERATURE

temperature considerably below the racking temperature, except for samples which were racked at 18° C. or lower. An unexpected result is that, according to Figure 1, those racked below 20° retract at 18.2° to 18.5° C. The phenomenon has the characteristics of a melting point.

[1] The authors are indebted to E J Joss for making these measurements.

In Figure 2, the curve exhibits the relationship between retraction temperature and racking temperature. The constancy of the retraction temperature for racking temperature below 18° C. is indicative of melting phenomena. Ordinarily, the melting point of a crystal is the temperature at which the crystal is in equilibrium with the liquid. In the case of racked rubber at 18° C. the phenomenon differs from the ordinary melting point in that a state resembling the crystalline state produced by elongation of the rubber changes to the liquid state, which is supercooled with respect to the ordinary crystalline rubber which melts at 35° C. (*6*). The two changes of state are similar in that heat is absorbed as the solid is transformed to the liquid state (*4*, *6*). Another peculiarity of the racked rubber is that the transition or retraction temperatures above 18° C. depend upon the temperature at which the racking was produced. These phenomena are, undoubtedly, correlated with the composition and structure of rubber and, eventually, should be useful in such interpretations.

T-50 VALUE OF UNVULCANIZED RUBBER

From the racking experiments, the authors have found a characteristic temperature, 18° C., for unvulcanized rubber which is a convenient reference point for comparison with vulcanized rubber, and which has been adopted as the T-50

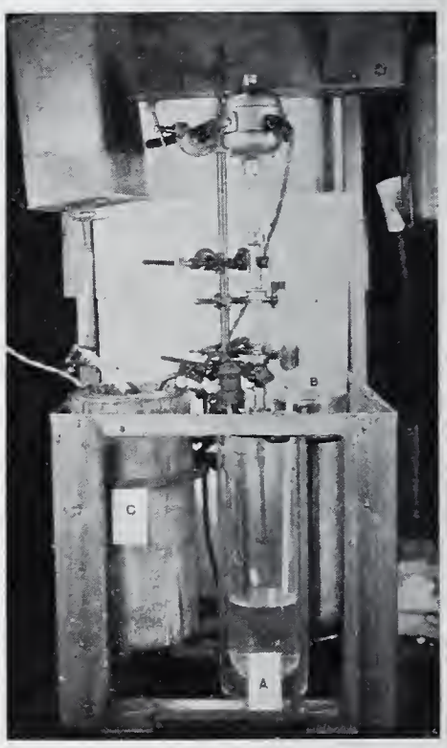

FIGURE 3. APPARATUS FOR T-50 TEST

value for unvulcanized rubber. This retraction temperature is decreased when vulcanized rubber is tested. Obviously, since the retraction temperature of unvulcanized rubber is influenced by racking at temperatures above 18° C., a test for state of cure above this temperature would not be satisfactory.

The T-50 value of unvulcanized rubber has been determined from the racking experiments and also by extrapolation of curve T-50 versus combined sulfur or time of cure to zero combined sulfur or time of cure. These methods agree substantially. In addition, the T-50 value of unvulcanized rubber has been determined directly for smoked sheet, latex thread, and sprayed rubber originally stretched at 700 per cent elongation, and found to be 16°, 17°, and 18° C.,

respectively. These differences are probably related to the permanent set of the rubber and are largely eliminated when vulcanized rubber is used, since the extrapolated T-50 value is 18° C.

Apparatus Used for T-50 Test

Testing Dewar and Fittings. An unsilvered Pyrex Dewar tube, called the testing Dewar, *A* (Figure 3), is mounted on a 30-inch (76-cm.) standard of 0.5-inch (1.3-cm.) iron rod. Supported in this tube are a stirrer, an electric heater, a thermometer, and a siphon tube. The stirrer is driven by a small electric motor, mounted on the standard; the speed is controlled by a variable resistance mounted in a convenient position. The current supplied to the heater is also controlled by a variable resistance. The toluene thermometer has a range of −90° to +50° C.

Figure 4. Rack for Holding Samples

Conditioning Dewar. To the right of the testing Dewar, another Dewar tube, called the conditioning Dewar, *B*, is mounted on the standard. This contains a thermometer (−10° to +100° C.) and a siphon tube.

Cooling Can and Coil. To the left of the testing Dewar, a double-walled copper can *C* is mounted. This contains a copper tube coil, one end of which is bent to deliver into the testing Dewar; the other end is connected by rubber tubing to a one-gallon (4-liter) can supported 1 or 2 feet (30 or 60 cm.) above it.

Mounting. The apparatus, except the variable resistances, is mounted on a wooden base 51 × 40 cm.; and is enclosed in a sheet-iron shield, with a window of Triplex glass in the front. The whole assembly can be placed on a table or bench.

Rack and Clamps. The rack for holding eight samples is a strip of brass about 30.6 × 6.38 cm. (Figure 4). A scale graduated in 0.1 inch is scratched on it. At the bottom is a clamp for holding the lower ends of the samples to be tested.

The upper clamps for died-out test pieces are individual, a separate clamp being used for each sample. Each clamp is attached to a length of silk cord, which has a glass bead strung on it, held in a fixed position by knots. The bead serves to hold the sample stretched at the desired elongation by engaging in a slot at the top of the rack. Attached to the top of the rack is a horizontal brass bar with grooves cut in it, to serve as guides to the clamp cords.

Figure 5 shows rubber test pieces in the Dewar in various stages of retraction. The long pieces are the short cures and the short pieces are the long cures. This illustrates the behavior of stock 29–92–I for 35, 40, 45, 50, 55, 60, 65, and 70-minute cures at 141.5° C. (40 pounds steam pressure).

Dies. Special dies are used for cutting test pieces from sheets. The dies cut pieces 0.19 cm. (0.075 inch) wide, with square tabs 0.638 × 0.638 cm. (0.25 × 0.25 inch) on each end. There are three sizes of dies, giving test pieces with 2.54 cm. (1 inch), 3.82 cm. (1.5 inches), and 5.08 cm. (2 inches) length of the narrow part. This is convenient when the sample is in the form of a sheet of fairly uniform thickness, 0.051 to 0.39 cm. (0.020 to 0.15 inch) gage.

Testing Procedure

The samples of rubber are brought to a definite temperature (0° or 20° C.) in a liquid bath, stretched to a predetermined elongation, and held at that elongation while they are dipped into a bath of chilled acetone in the testing Dewar. After the temperature of −70° C. has been attained, the samples are released; they do not contract, however, but take on an almost complete set. The temperature of the bath in the testing Dewar is slowly raised; the samples contract as the temperature rises. The temperature at which the elongation of each sample is 50 per cent of the original elongation is noted as the T-50 value for the sample.

Preparation and Racking of Samples. Samples are died out with a special die. One end of each test piece is held in the clamp at the bottom of the rack, while the other end is held in an individual clamp, with silk cord attached. The cords are led through the slots at the top of the rack and down behind the rack.

Filling the Cooling Can. The cooling can is filled with about 4 pounds (1.8 kg.) of pulverized solid carbon dioxide. Acetone, a little at a time, is cautiously poured into the can, stirring with a wooden rod, until the mixture forms a thick slush. More dry ice and acetone are added until the can is filled to a point about 2.5 cm. from the top, and the mixture is tamped down so that it completely surrounds the cooling coil.

The clamp is closed on the rubber tube, which connects the reservoir with the cooling coil, and about 0.5 gallon (2 liters) of acetone is put into the reservoir.

Conditioning the Samples. The procedure for this step differs slightly according to the stock being tested.

For unaccelerated gum stock, the conditioning Dewar is filled with ice water containing a little finely crushed ice, and the rack containing samples is placed in the Dewar and allowed to stand for 1 minute. The temperature should be 0° C. After 1 minute, the samples are stretched to the required elongation, and held there by engaging the beads on the upper clamp cords in the slots at the top of the rack. The cords are led over the guiding grooves in the bar at the top of the rack, and down outside the Dewar tube. The time when the last sample is stretched should be noted. Samples should remain stretched for 5 to 6 minutes before transferring to the testing Dewar as described below.

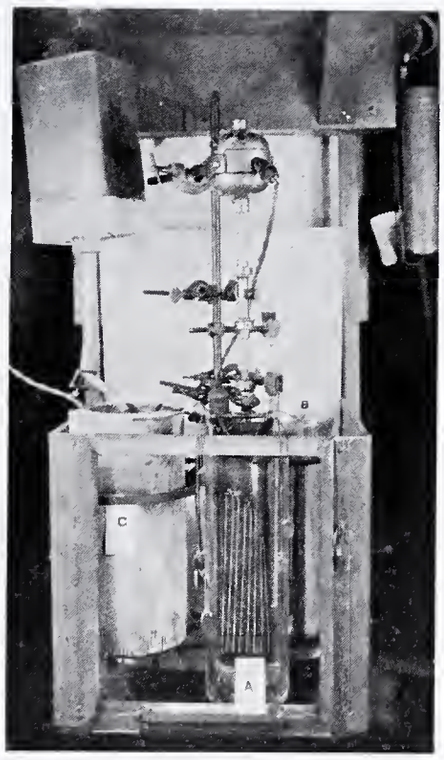

Figure 5. Apparatus Showing Test Pieces in Various Stages of Retraction

For accelerated gum stock, the conditioning Dewar is filled with acetone at 20° ± 0.2° C. For tread or other highly compounded stock, water at 20° C. is used.

Filling the Testing Dewar. About 3 minutes after stretching the samples, the pinchcock on the rubber tube between the reservoir and the copper coil is opened, and the testing Dewar is filled with cold acetone to within 1.25 cm. of the top. This takes about 1 minute.

Transferring Samples. Five minutes after stretching the samples, the rack is transferred quickly to the testing Dewar, and the stirrer started and let stand about 1 minute in order to attain temperature equilibrium. The temperature of the conditioning bath is read and recorded. If the rack was immersed in a conditioning bath of ice water, this is rinsed off with acetone at a temperature below 0° C. before putting the rack in the testing Dewar.

Refilling Testing Dewar. The liquid in the testing Dewar is siphoned off and poured back into the reservoir, and the testing Dewar refilled as in first filling. While refilling, the length of

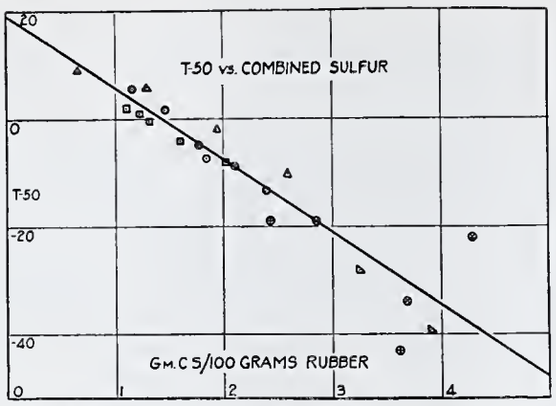

Figure 6. T-50 Values *vs.* Combined Sulfur

each sample in the stretched condition is read and recorded as L_S. The refilling operation is repeated until the temperature falls to −70° C. or lower. Inability to reach this temperature is usually due to an insufficient supply of solid carbon dioxide in the cooling can.

Freezing Temperature. The stirrer is started, and after 1 minute the temperature is read and recorded as the freezing temperature (T_f).

Releasing Samples. Immediately after reaching T_f, the samples are released by pushing the beads free from notches. As quickly as possible, the length of each sample (L_1) and the temperature at which the length was read (T_1) are read and recorded. In reading the length of a sample, the sample is pulled taut, but not stretched, by means of the upper clamp cord.

Calculation of L_{50}. For each sample, the length at which the elongation is 50 per cent of the original elongation is calculated, and recorded on the data sheet as L_{50}. It is easily seen that

$$L_{50} = \frac{L_1 + L_0}{2}$$

L_1 = length of stretched sample
L_0 = original length of unstretched sample

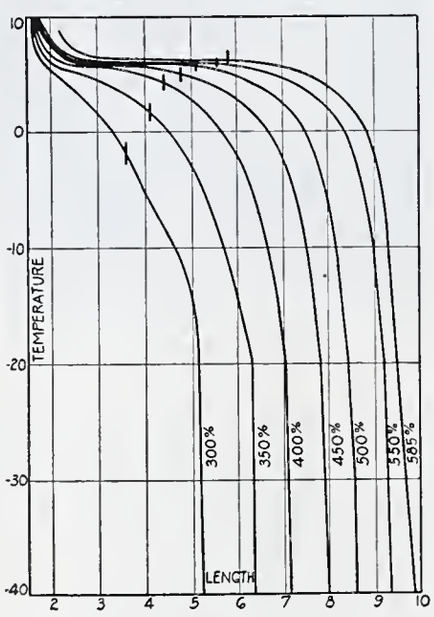

Figure 7. Length of Rubber Given Different Initial Elongations, as Function of Temperature

Determination of T-50. The remainder of the test consists in determining T-50, the temperature at which the sample reaches the length L_{50}. In some cases (unaccelerated stocks) the rubber contracts gradually at a more or less uniform rate as the temperature rises; in other cases (accelerated stocks) very little contraction occurs until a certain temperature is reached, when a sudden large contraction takes place. To determine the T-50 value accurately, especially in the case of unaccelerated stocks, the rubber must be heated slowly in the vicinity of T-50. The length of the rubber does not change when held at constant temperature, and when the temperature is increased the length becomes constant practically as soon as the test piece comes to thermal equilibrium with the bath.

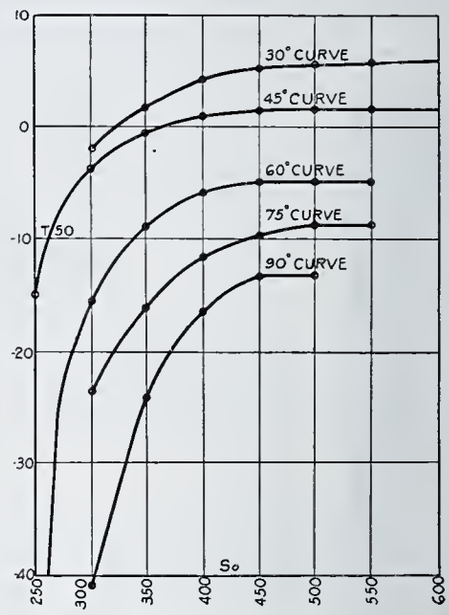

Figure 8. T-50 Values Plotted as Function of Initial Elongation

The heater resistance should be adjusted to give a rise of temperature of about 5° C. per minute. After heating at this rate until within about 10° C. of T-50, the heater resistance is readjusted to slow down the rate of heating to 1° C. per minute or less. If the T-50 value is not known beforehand within 10° C., the rapid rate of heating must be discontinued before there is any danger of reaching T-50. The temperature at which the sample reaches the length L_{50} is noted, and recorded as the T-50 value. When reading the length, the sample should be held taut but not stretched.

Table I. Conditions of Testing for Different Types of Stocks

Stock	Conditioning Bath and Temperature	Length of Test-Piece		Elongation
		Cm.	(*In.*)	%
Unaccelerated gum	Water at 0° C.	2.54	(1)	650
Accelerated gum	Acetone at 20° C.	3.81	(1.5)	500
Tread stock and other highly compounded stocks	Water at 20° C.	5.08	(2.0)	350

Experimental Data

In Figure 6 are shown the T-50 values of five different accelerated gum stocks plotted as ordinates and grams of combined sulfur per 100 grams of rubber as abscissas. A straight line was drawn through the points, showing that there is a general correlation between T-50 and combined sulfur. The chemical analyses (*5*) were made in the usual manner by analysis of the acetone-extracted rubber and were not corrected for sulfur combined with zinc oxide or other non-rubber constituents. The cause of the imperfect correlation is not known. This point has not been pushed to a definite conclusion, since the test was developed primarily as a measure of state of cure for a specific compound. It is satisfactory in this respect, since from a series of cures it

consistently selects a given cure. The time consumed in making a T-50 run varies from 30 to 60 minutes.

In Figure 7 is shown the length of a piece of rubber, compound 29–92–I, which was given different initial elongations, L_1, in the conditioning bath, as a function of temperature in the testing Dewar. This stock was prepared as follows: Smoked sheets, 100.0; sulfur, 3.0; zinc oxide, 5.0; hexamethylenetetramine, 1.125; and VGB (antioxidant), 1.0. It was cured 30 minutes at 141.5° C. (40 pounds steam pressure).

The T-50 values, indicated on each curve, approach a constant value as the initial elongation, L_1, is increased, showing that it is necessary to employ sufficient elongation or the T-50 value will be too low and the extent of cure will appear too great.

In Figure 8, the T-50 values for a series of cures of compound 29–92–I are plotted as a function of initial elongation, S_0. This plot also serves to illustrate again for different cures how the T-50 value approaches a constant value at sufficient elongation.

Uses of Test

The T-50 test has been applied to many types of rubber compounds—smoked sheets, crepes, Para, reclaim, sprayed and latex rubber—using various fillers. The filler lithopone contains sulfur in varying amounts, making chemical analysis for combined sulfur difficult. The T-50 test simplified the estimation of state of cure, but is limited to those types of rubber which can be stretched. Thus, hard rubber, sole, tile, and heavily compounded compounds are not suitable. Carbon blacks vary in their effect on rate of cure. The test has been used to detect differences in rate of cure and to test activity of accelerators. The state of vulcanization depends upon the temperature of the rubber compound during vulcanization, and the length of time during which it is held at that temperature. In actual practice there are variables such as temperature of presses, mold lag, and differences in temperature of the top and bottom sides of the mold. The effect of these variables on state of cure can be evaluated by the test. In many laboratory tests designed to test rubber for resistance to some service condition, such as abrasion or flexing, it is much easier to interpret the results if the state of cure of the test piece is known.

The test has the advantage over tensile tests in that the width and thickness of the test piece need not be measured, but on the other hand it does not select optimum cures or the state of cure in a series of cures which will resist deterioration or abrasion. These properties must be determined independently. The utility of the test consists in the determination of the state of cure independent of physical properties which depend upon the composition.

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Recommendations for Use of a 26.026-Gram Normal Weight for Ventzke Scale Saccharimeters

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THE recognition of a long-established error of 0.1° in the 100° point of Ventzke scale saccharimeters by the International Commission for Uniform Methods of Sugar Analysis at its eighth session, held at Amsterdam, September 5 to 8, 1932, was most fortunate in removing the uncertainties which had prevailed among the users of Ventzke scale saccharimeters in all parts of the world.

Among the recommendations of the commission, adopted at the Amsterdam meeting, is the following:

> In the case of existing instruments graduated on the Herzfeld-Schönrock scale (i. e., Ventzke scale) it shall be permitted either to change the saccharimeter scale or to use a weight of 26.026 grams in 100 ml.

The old Mohr cc. normal weight for Ventzke scale saccharimeters was 26.048 grams and some users of saccharimeters still employ this old standard. In order to avoid the error which might result from the mistaken use of the old Mohr cc. normal weight in place of the metric cc. normal weight of 26.000 grams, which was adopted by the commission at its Paris meeting in 1900, manufacturers of weights adopted a cubical form for the metric cc., or ml., weight which could be readily distinguished from the old cylindrical Mohr cc. weight. In view of the alternative suggestion of the commission to employ a new normal weight of 26.026 grams for correcting the error of the old Ventzke scale, it would seem desirable that such weights should have a shape that is readily distinguishable from the older forms. The writers have accordingly had constructed hexagonal weights of brass for the new normal and half-normal values of 26.026 and 13.013 grams, respectively. As an additional protection against confusion, the new weights have their numerical value in grams stamped upon the upper surface. The stems of the weights can be unscrewed if it is desired to correct any slight loss from abrasion by the insertion of a small thread of wire in the interior cavity.

This method of correcting the error of the old Ventzke scale necessitates no change in the instrument and is much cheaper and fully as accurate as to equip saccharimeters with special new scales which would correspond with the former normal weight of 26.000 grams. By supplying new weights manufacturers will render a much needed service to the many thousands of chemists who are using saccharimeters of the old Ventzke scale type.

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A Simple Large-Capacity Extractor

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NEED for an extractor of the Soxhlet type which could be operated with a charge of approximately 10 pounds of ground roots or seeds prompted the design of the apparatus shown in Figure 1. This extractor can be constructed at low cost, is relatively durable, absolutely free from any fire hazard, and can be assembled from material generally available in the laboratory. Although designed primarily for use with methanol, it could be used with few changes for any solvent boiling below 100° C.

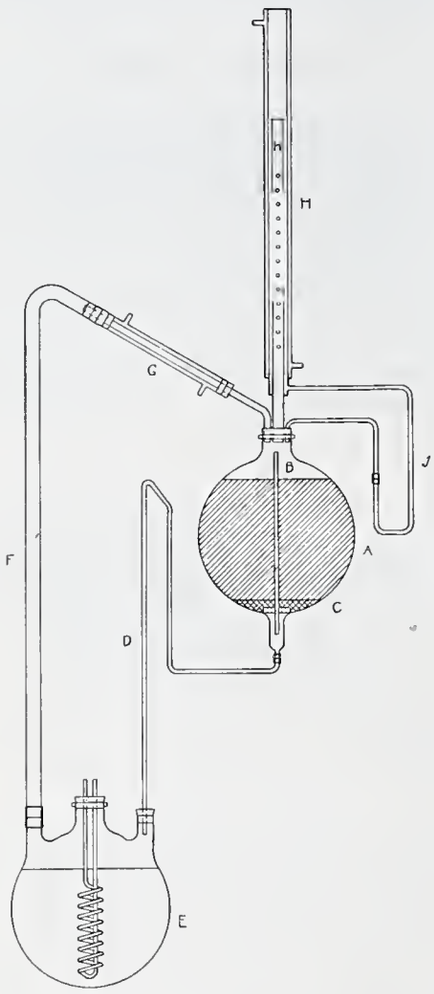

Figure 1

A 12-liter short-necked Pyrex flask, *A*, serves as the extractor body. To the bottom of this flask is sealed a 3-in. (7.5-cm.) length of 25-mm. tubing which ends in a short piece of 5-mm. tubing, and serves as an adapter for connecting the siphon tube which returns the solution to the boiler. Connection between the extractor and the glass siphon tube is made by rubber tubing within which there is a glass-to-glass contact. A large thin cork bored in the center to hold the breather tube, *B*, and pierced with several holes to allow free passage of solvent, serves to support a thin layer of absorbent cotton, *C*, upon which rests the material to be extracted. The broad cotton surface promotes rapid draining and effectively filters the returning solvent. The breather tube promotes clean siphoning by eliminating the resistance of the marc to the passage of air. The return siphon, *D*, is of 5-mm. tubing, connected to the boiler through a rubber stopper and to the extractor as described above.

The boiler, *E*, is a 12-liter, three-necked Pyrex distilling flask. One small neck serves to admit the returning solution and the other to conduct solvent vapor to the condensers. The large neck is closed by a rubber stopper through which pass the inlet and outlet of a small copper steam coil. Such a heating coil can be easily constructed by winding 0.25-in. (0.62-cm.) outside diameter copper tubing on a piece of iron pipe of suitable diameter. Inlet and outlet can then be attached by soldering 0.125-in. (0.3-cm.) brass pipe nipples of appropriate length to the ends of the copper coil. The outlet of the heating coil is not throttled during operation so that there is little pressure within the coil. A suitable steam valve on the inlet controls the steam flow. Solvents whose boiling points are below 100° C. can be boiled very conveniently in the apparatus without the slightest fire hazard.

The riser tube, *F*, ends in a short partial condenser, *G*, constructed from a piece of 0.5-in. (1.3-cm.) outside diameter copper tubing with a glass water jacket. This condenser discharges into flask *A* through a triply bored stopper. Through the other holes in this stopper pass the vapor tube of the total condenser, *H*, and its solvent return line.

Condenser *H* is similar to a glass condenser described by Cameron (*1*). It is constructed entirely of metal, and can be easily assembled from standard copper tubing. The vapor inlet tube, *h*, is capped at the end and pierced by a number of small holes. Solvent vapor passes through these holes and impinges on the cold wall of the condenser. The resulting condensate flows down through the small annular space between the vapor riser tube and the condenser wall to the bottom of the condenser, whence it returns through trap *j* to flask *A*. The return trap, *j*, is of glass, connected to a metal nipple soldered to the condenser by means of a rubber joint. A condenser of this type is free from the disadvantage of flooding even when used at very high condensation rates. When methanol is used as solvent, siphoning takes place every 45 minutes.

The connection between boiler and partial condenser is made of Pyrex tubing of suitable diameter, jacketed with asbestos. A bored stopper affords a means of connection at the condenser end, and a tightly fitting rubber tube within which there is glass-to-glass contact makes the joint to the boiler.

During operation it is not necessary to move boiler or vapor riser tube. The extractor body can be detached from the rest of the apparatus for charging and discharging, and solvent can easily be removed from the boiler by siphoning. In the authors' apparatus a pipe union makes it possible to break the steam inlet lines, and consequently the steam coil can be lifted from the boiler for convenience in siphoning off its contents.

An apparatus like the one described has been in operation constantly for several months and has proved highly satisfactory in every respect.

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Received April 5, 1933.

Laboratory Apparatus for Producing a Controlled Temperature Program

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In connection with studies of the influence of the rate of heating in the carbonization of coal, a control system has been developed to procure definite, predetermined, and reproducible rates of temperature rise in an electric furnace, and to provide a record of the actual temperature at all times. The design of the apparatus is relatively simple, permitting it to be constructed from readily available parts, and the control mechanism has great flexibility so that it may be used for many purposes.

In the particular application of the control apparatus to be described, its performance has been satisfactory during 2 years of operation. The temperature of a furnace, drawing as high as 2250 watts at 110 volts, has been raised from room temperature to 1000° C. in 3, 6, 12, and 24 hours, respectively, at constant rate throughout, and the temperature subsequently maintained constant at 1000° C. for 1 hour. The recorded temperature never departed from the predetermined temperature at any instant by more than 10° C. Since the retort in the furnace has a fairly high heat capacity, the variation of the retort temperature itself was somewhat less.

A diagrammatic sketch of the apparatus used is shown in Figure 1. The furnace temperature is measured by a thermocouple and recorded on the chart of a standard recording potentiometer. The controller is built onto the recorder as an integral part and consists essentially of a mandril, a control chart, two brushes, and a stylus. The mandril is identical with that which carries the chart under the recording pen and is supported so that both mandrils are rotated by the recorder-driving mechanism. The control chart is carried by this mandril and is constructed from a portion of the recorder chart by first drawing upon it the desired time-temperature curve and then cementing onto the paper strips of aluminum foil in such manner that the time-temperature curve lies in a slit 0.06 inch (0.16 cm.) wide between strips of foil. (Artists' rubber cement has proved a very convenient adhesive, as it does not wrinkle the paper. Good electrical contact was obtained between two foil strips cemented together with it, in spite of the rubber.) To each of these strips is connected a second strip which is 1 inch (2.5 cm.) wide, laid along the adjacent edge of the paper parallel to the time axis. The brushes are supported above and make contact with the control chart through the marginal strips. The stylus is also supported above the control chart and is moved parallel to the temperature axis by the same mechanism which moves the recording pen, so that it will lie in the slit or on one or the other of the foil strips, depending upon the temperature and the time. Two relays, one connected to each brush and to a source of potential through the stylus, complete the set-up.

In use the control chart is placed upon its mandril at zero time reading, the brushes and stylus are lowered upon it, power is turned on to the furnace, and the recorder motor is started. The recorder pen and the stylus moving with it then take up a position which indicates the temperature. If this is the proper temperature for this instant of the program, the stylus will lie on the slit between the foil strips and will not make contact with either; thus, neither relay is actuated and a medium value of current is provided by the shunt around resistance R_3 and part of R_2. If the temperature continues to rise according to the desired program, the stylus will move so as always to lie on the slit as the chart is moved forward. However, if at any given time the temperature is too low, the stylus will make contact with the left-hand or low-temperature foil, completing the circuit through the battery to relay 1, and thereby causing an increase in current, since the shunt around R_3, R_2, and part of R_1 is completed through closing C_1. Likewise, if the temperature is too high, contact will be established between the stylus and the right-hand or high-temperature foil, completing the circuit through the battery to relay 2, opening C_2 while C_1 remains open and thus providing a decrease in current, since both shunts are open and the only path for current is through R_3, R_2, and part of R_1. Therefore, the system operates so as automatically and continuously to choose one of three graded values of current according to the instantaneous requirements of the program.

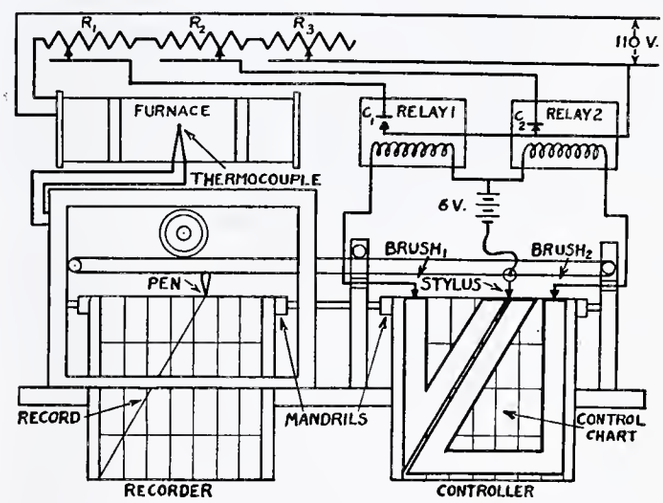

Figure 1. Diagram of Apparatus

In practice the low value of current is chosen, through adjustment of R_3, such that the required rate cannot be maintained even at lowest temperature, while the high value is chosen, through adjustment of R_1, so that the rate of rise will be too rapid even at highest temperature. The medium value is then set half way between by adjustment of R_2. In the case of the author's furnace of 6-ohm resistance, 5, 10, and 15 amperes were the values used for a program of 6 hours to 1000° C. This use of three different controlling conditions is particularly valuable where the range of temperature over which the controller operates is great, since thereby "hunting" is considerably reduced. In case of a narrower range of temperature it is possible that the edge of a single foil strip and one relay, hence two controlling conditions, would suffice. As a matter of fact, it is observed that during the early part of a program, the system alternates between the low and medium currents and toward the end between the medium and high currents, while during an intermediate range of temperature three values of current are used.

In the above paragraphs an apparatus has been described

for controlling the rate of heating of an electric furnace over the temperature interval from room temperature to 1000° C. However, the control system is not limited to this use but may be adapted to procure any desired temperature program or to control the rate of heating or cooling in metallurgical and chemical problems, wherever the method of adding or removing energy can be controlled by operation of electrical relays. While the description of the apparatus and its use has been limited to programs involving temperature as a function of time, it appears evident that only slight modifications would be necessary to use the same system for controlling other variables as a function of time.

Received March 29, 1933.

A Microextractor

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IN CONJUNCTION with the biological and chemical study of the inland lakes of Wisconsin conducted by the Geological and Natural History Survey under the direction of E. A. Birge and C. Juday, it was found desirable to determine the ether extract of the lake water residues prepared by the evaporation of known volumes of water. Since the water of a large number of the lakes was soft, it was not convenient to prepare large residues, for this in turn would require the evaporation of large quantities of water. It was therefore necessary to select an extraction method which was applicable to small samples.

The macro-Soxhlet could not be used and early study was directed toward the use of a small-size Soxhlet extractor, as shown in Figure 1. The siphon *C* measures 4 cm. from the seal to its top and functions when it contains 8 cc. The extraction thimble was made by sealing a porous alundum disk into a section of glass tubing, *X*. A 15-mg. dried sample of lake residue was transferred to the thimble, 15 cc. of dry redistilled ether were placed in the flask, and the ether was refluxed over the sample for 24 hours. The flask *Y* was then placed over fused calcium chloride in a vacuum desiccator and the ether removed by evaporation. After the flask and extract had dried in this system for 12 hours, the flask was allowed to stand in the balance for 15 minutes and weighed. The increase in weight of the flask represented the weight of the extract.

Although this system proved satisfactory, particularly for samples containing a reasonable amount of extractive material, certain difficulties appeared which made an extension of the study imperative. The purpose of the present paper is to describe a new microapparatus and procedure which developed from a study of these difficulties.

New Microapparatus

The condenser and lower part of the extractor shown in Figure 2 are of Pyrex glass. The lower part, *S*, was blown from a standard Eck and Krebs 40-mm. joint, the outer member of the joint, *R*, sealed to the condenser, and the tube of the inner member *A* sealed to form a cup.

The extraction thimble *T* is made from a 16-mm. Pyrex tube. The inner part of the joint shown in the diagram is made by grinding the end of a short section of 15-mm. tube to fit inside the end of the longer 16-mm. tube. Hooks are sealed on the top of the thimble to support it on the aluminum ring *E*. An 18-mm. disk of filter paper is cut from larger sections of Whatman No. 50 or S. and S. No. 575. The disk is wet with water, laid over the ground end of the outer tube of the thimble, and forced into place by firmly pressing the inner ring into the ground end of the larger tube, thereby closing the bottom of the larger tube with paper. It is important that the surfaces of the joint be very carefully ground so that when the paper is in place finely divided particles of sample cannot leak through the joint.

The weighing bottle *D* was blown from soft glass and has a total weight of 4 grams. When the bottle is in position in the extractor, the clearance between the bottle and the thimble is at least 1 mm.

The outer joint of the extractor is dry and must be ether-tight in order that extraction may proceed at reduced pressure without the loss of ether. In earlier models, a mercury seal was provided to prevent loss of ether at the joint, but this has since been eliminated. In order to prevent condensation of ether at the joint, it is necessary to provide a moderate amount of heat. This is accomplished by passing one strand of No. 26 nichrome wire around the top of the joint at *P*, fastening it by means of adhesive tape, and maintaining a temperature of about 50° C. by making an alternating current connection and adjusting the resistance in the line (contribution by Walter Militzer, limnology assistant). The adhesive tape must cover the wire in order to keep the joint warm.

Suction. An ordinary water pump is used to reduce the pressure in the apparatus. The connection is made from the pump to an expansion flask, to the manometer, and finally to the extractor. A plug of cotton is placed in the outlet of the extractor so that dirt cannot be drawn into the extractor when the stopcock is opened at the end of the extraction procedure. Connection may be so arranged that the one pump and manometer will serve several extractors. (The authors use a battery of six extractors.)

Heating. The extractor is heated by means of a 40-watt lamp placed in a small box which is covered with an asbestos board. The top of the box has a 3-inch (8-cm.) opening which makes it possible to place the extractor close enough to the lamp to provide the proper rate of distillation.

Ether. Ethyl ether was allowed to stand over fused calcium chloride for 2 weeks and finally distilled. Metallic sodium was added to the distillate and the dry ether was then distilled as needed. The fraction distilling between 34° and 36° C. was used in the extractor. Thirty cubic centimeters of the freshly distilled ether gave no detectable residue upon evaporation.

Procedure

Before beginning a determination of ether extract, the entire apparatus is cleaned thoroughly with "cleaning solution" and finally rinsed with water, alcohol, and ether in the order named. The apparatus, with the exception of the thimble *T* and weighing dish *D*, then needs no further cleaning between determinations, since nothing but ether vapor comes in contact with it. The weighing dish *D* is cleaned in a similar manner, and dried in a vacuum desiccator over fused

calcium chloride at room temperature for 2 hours. It is transferred to the microbalance, where it is allowed to stand until it reaches equilibrium before it is weighed. The time required to bring the bottle to equilibrium must be determined. It is usually about half an hour.

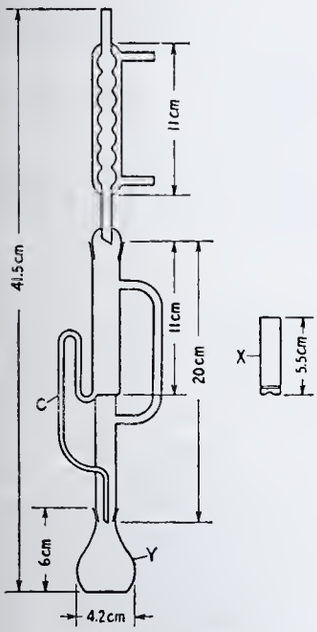

FIGURE 1. MICRO-SOXHLET EXTRACTOR

The glass parts of the thimble are cleaned in a similar manner, and when the wet paper disk is pressed into position the thimble is again washed with alcohol and ether and allowed to dry. In the analysis of fat samples, the thimble was taken apart and the fat was weighed directly on the paper disk. However, in the case of the dry finely divided samples, the thimble was assembled and the weighed sample introduced at the top. The introduction of the sample into the thimble is facilitated by the use of a small trough-like piece of cut tube as the weighing glass.

After transferring the sample to the thimble, 5 cc. of ether are added to the previously tared weighing bottle and the bottle placed in the bottom part of the extractor. The aluminum ring *E* is then placed on the top edge of *A* and the thimble is lowered into position until the hooks of the thimble are supported on the aluminum ring. A few drops of ether are now poured through the thimble to wash down any stray particles which may have lodged on the walls of the thimble. The cup *A* is then joined to the upper part of the extractor.

The apparatus is evacuated to a pressure of about 20 cm. of mercury and the stopcock is closed. The current for the heating lamp and the heating wire at the extractor joint is turned on and extraction begins. The extractor is adjusted at such a distance above the lamp that the rate of condensation of the ether is not fast enough to cause the ether to rise above the constriction in the thimble. (In the summer time, the tap water may be warm and to insure rapid condensation the water is allowed to run through a cooling coil before passing to the condenser.)

After 23 hours of extraction, the vacuum pump is started and the stopcock gradually opened. Evacuation is continued until all the ether has disappeared. Air is then carefully admitted to the apparatus until atmospheric pressure is reached. The lower part of the extractor is removed and the weighing bottle transferred to the vacuum desiccator where it is allowed to stand over calcium chloride for 2 hours. The bottle is then transferred to the microbalance, allowed to come to equilibrium, and weighed. The increase in weight of the bottle is the weight of the extract.

Two weighing bottles and two thimbles were prepared for each extractor, so that while one set is in use the other may be cleaned and weighed. One hour is ample time for removing the old sample and adding the new one and it therefore is possible to make one determination each 24 hours for each extractor.

RESULTS OF EXTRACTION

In order to test the operation of the extractor, samples were examined in the microextractor and the results obtained compared to those of the macro-Soxhlet extractor. Some representative results are given in Table I.

TABLE I. RESULTS WITH MACRO- AND MICROEXTRACTORS

SAMPLE	ETHER EXTRACTS Macro	Micro
	%	%
Dry skim milk	0.08	0.07
	0.08	0.09
Casein	0.16	0.16
	0.15	0.19
Feed sample 439	5.0	5.43
	..	5.45

One to seven milligram samples of pure lard were weighed into the extraction thimbles and upon extraction recovery was obtained within ±0.002 mg. The following results illustrate the degree of agreement between duplicate samples of lake water residues.

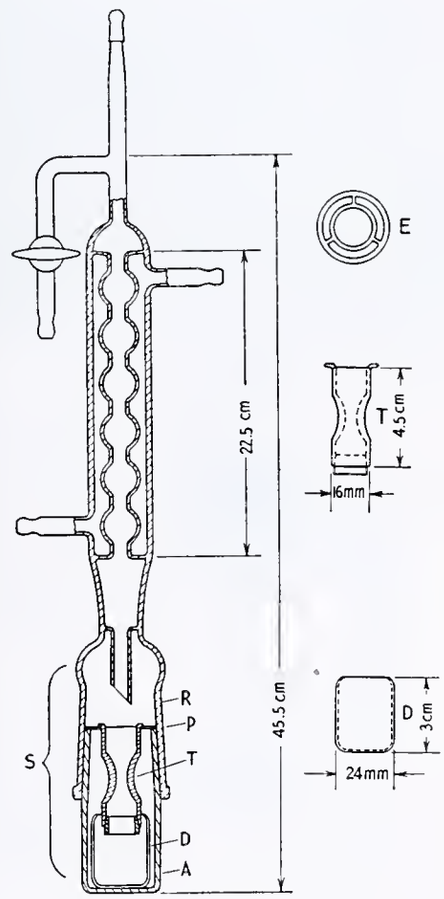

FIGURE 2. NEW MICROEXTRACTOR

TABLE II. EXTRACTION OF LAKE WATER RESIDUES

SAMPLE	WEIGHT OF SAMPLE	WEIGHT OF EXTRACT	
	Mg.	*Mg.*	%
Upper Gresham	15.671	0.164	1.05
	12.785	0.138	1.08
Clear Crooked	14.903	0.219	1.47
	13.800	0.205	1.49
Crystal	10.603	0.037	0.35
	13.605	0.050	0.37

DISCUSSION

In using the direct extraction apparatus, the difficulties encountered with the micro-Soxhlet apparatus have been greatly minimized or entirely eliminated. The final evaporation of the solvent in the micro-Soxhlet required the removal of the 25-cc. weighing flask to the desiccator and sometimes the complete transfer of the ether extract to a smaller dish

preliminary to evaporation and weighing. In the new apparatus, the weighing bottle is not moved until all the solvent has been evaporated. Possible mechanical loss is avoided. The fact that the new weighing bottle weighs only 4 grams probably improves the chances of weighing with a precision of ±0.001 mg.

In the micro-Soxhlet apparatus, the extraction thimble was made by sealing an alundum disk into a section of glass tube *X*. It was difficult to select an alundum disk whose pores were sufficiently small to retain finely divided sample and at the same time allow the ether to flow through at a reasonable speed. The straight walls of the original thimbles also allowed occasional small sample losses due to creeping. The new thimbles eliminated the first difficulty by the substitution of the paper disk and the second difficulty by a constriction of the walls of the thimble *T*. There is little doubt that operation at reduced pressure also prevented creeping of the solvent to some extent. Upon condensation the ether flows into the thimble and directly into the weighing bottle. No ether collects in the bottom or at the joint of the extractor. If ether is lost during the extraction, an additional aliquot may be added at the top of the condenser without disturbing the sample.

While ether is the only solvent mentioned in this investigation, it is possible to use other reagents effectively.

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A Simple Laboratory Tachometer

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A TACHOMETER, or angular velocity indicator, can occasionally be used to excellent advantage in the laboratory—for instance, in the control of high-speed agitators in process work, to give warning of viscosity changes in the contents of autoclaves, or to secure reproducible agitation conditions in analytical procedures.

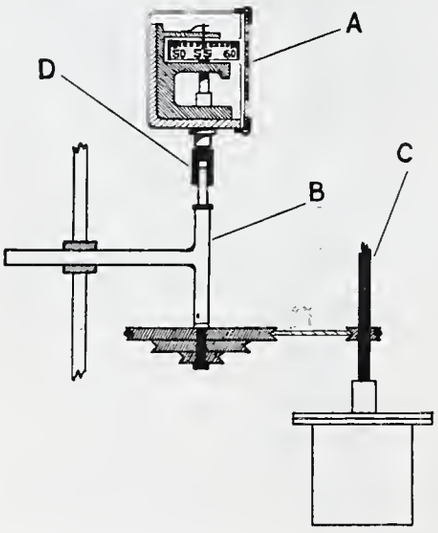

Figure 1. Connection of Tachometer to Drive Shaft

A, old speedometer with mileage counter removed
B, inverted agitator drive
C, shaft of high-speed agitator, line shaft, or other mechanism
D, rubber tubing

There are commercial instruments adaptable to these uses but they are complicated, expensive, and of unnecessary precision for this type of work (*1*). It has been found that a very inexpensive device can be constructed from a salvaged automobile speedometer. The magnetic type of instrument is convenient to convert, as it is merely necessary to remove the mileage counter to avoid excessive drag on the drive shaft, thereby rendering the instrument more sensitive. If the tachometer is to be attached to a permanent set-up, it may be connected directly to the shaft whose velocity it is desired to obtain by means of flexible shafting and suitable gears. A more useful method is to invert an ordinary agitator-drive, connecting the speedometer shaft to the clutch end of the latter with a short piece of rubber tubing. The instrument is then operated by a belt and a properly selected set of pulleys. This arrangement provides for a wide range of angular velocities falling within the limits of the speedometer scale. It has been found that under ordinary conditions belt slippage is practically undetectable.

The scale reading may be correlated to the angular velocity of the driving shaft by the use of a variable-speed motor or some other method for changing the velocity of the driving shaft. Measurements of the angular velocity of the motor shaft are conveniently taken with a revolution counter, at the same time noting the tachometer reading at different speeds, and the data so obtained are plotted on coördinate paper. The velocity of the drive shaft may then be picked from the curve at corresponding tachometer readings.

An alternative scheme is to adjust the pulley diameters so that the speedometer scale may be read directly in revolutions per minute, or in decimal multiples thereof. For example, on a high-speed agitator used by the writer a scale reading of 40 indicated a shaft velocity of 4000 r. p. m.

Literature Cited

(1) Holder, L. F., *Gen. Elec. Rev.*, 34, 141 (1932).

Received April 24, 1933.

World Nitrogen Production Capacity for 1932–33, according to a German nitrogen director was:

		Per Cent
Atmospheric nitrogen:		
Synthetic ammonia process:		66.1
Haber-Bosch	33.15	
Casale	10.00	
Fauser	8.10	
Claude	4.40	
N. E. C.	3.90	
Mont-Cenis	3.80	
Shibata (Japan)	0.05	
F. N. R. L.	0.10	
Unknown	0.15	
Cyanamide		10.3
Arc		0.7
By-product ammonia		11.9
Chilean nitrate		11.0

The plants employing the major processes are: Haber-Bosch, 8; Casale, 26; Fauser, 16; Claude, 19; N. E. C. 15; Mont-Cenis, 7; and Cyanamide, 59.

Recommended Specifications for Analytical Reagent Chemicals

Benzoic, Boric, Formic, Sulfanilic, and Sulfurous Acids, Aniline, Hydrogen Peroxide, Mercuric Bromide, Potassium Biphthalate, Potassium Oxalate, Sodium Sulfite Anhydrous

W. D. Collins, H. V. Farr, J. V. Freeman, R. A. Osborn, Joseph Rosin, E. Wichers, and H. H. Willard

Committee on Analytical Reagents, American Chemical Society

THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for the improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications (*1–10*) from the committee. Directions for the preparation of the ammonium molybdate solution are given under the test for phosphate in ammonium nitrate (*3*). A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Blank tests must be made on water and all reagents used in the tests unless the directions provide for elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

ACID BENZOIC

Requirements

Melting Point—122° to 123° C.

Nonvolatile Matter—Not more than 0.010 per cent.

Solution in Ammonium Hydroxide—To pass test.

Chlorine Compounds (as Cl)—To pass test (limit about 0.001 per cent).

Sulfur Compounds (as S)—Not more than 0.001 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Tests

Melting Point—Determine according to the directions of the U. S. Pharmacopeia. When these directions are followed the initial melting point, that at which the material collapses in the tube, should be at least 122° and the point at which it is all melted should be not over 123° C.

Nonvolatile Matter—Heat 5 grams in a platinum dish at a temperature sufficient to volatilize the acid slowly but not to char or ignite it. When nearly all of the acid has volatilized add a few drops of sulfuric acid and ignite gently. The weight of the residue should not exceed 0.0005 gram.

Solution in Ammonium Hydroxide—Dissolve 2 grams in a mixture of 15 cc. of warm water and 5 cc. of ammonium hydroxide. No visible residue should remain.

Chlorine Compounds—Mix 1 gram with 0.5 gram of sodium carbonate and add 10 to 15 cc. of water. Evaporate on the steam bath and ignite until the mass is thoroughly charred, avoiding an unduly high temperature. Extract the fusion with 10 cc. of water and 1.5 cc. of nitric acid. Filter, wash, make to a volume of 25 to 30 cc., and add 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Sulfur Compounds—Mix 2 grams with 1.5 grams of sodium carbonate and dissolve in water. Evaporate to dryness and char thoroughly with a flame free from sulfur. Treat with 25 cc. of water, add a few cubic centimeters of saturated bromine water, and heat on the steam bath for 15 minutes. Neutralize with hydrochloric acid, adding a slight excess of the acid, boil gently to expel the bromine, filter, and wash. Add to the filtrate, which should measure about 25 cc., 2 cc. of 10 per cent barium chloride solution. The turbidity should not be greater than is produced by 0.06 mg. of sulfate ion in an equal volume with the quantities of reagents used in the test.

Heavy Metals—To the solution prepared for the test for solution in ammonium hydroxide add 5 cc. of hydrogen sulfide water. No darkening should be observed.

ACID BORIC

Requirements

Insoluble in Alcohol—To pass test.

Nonvolatile with Methanol—To pass test (limit about 0.05 per cent).

Chloride (Cl)—Not more than 0.002 per cent.

Phosphate (PO_4)—Not more than 0.001 per cent.

Sulfate (SO_4)—Not more than 0.010 per cent.

Arsenic (As)—Not more than 0.0005 per cent.

Calcium (Ca)—To pass test (limit about 0.005 per cent).

Heavy Metals—To pass test (limit about 0.001 per cent as lead).

Iron (Fe)—Not more than 0.001 per cent.

Tests

Insoluble in Alcohol—Heat 2 grams with 20 cc. of alcohol under a reflux condenser until the acid is dissolved. The solution, while hot, should be clear with no insoluble residue.

Nonvolatile with Methanol—Dissolve 2 grams of the powdered acid in 25 cc. of methanol and 5 drops of hydrochloric acid in a platinum dish and evaporate to dryness. Add 15 cc. of methanol and 3 drops of hydrochloric acid and repeat the evaporation. Add 2 to 3 drops of sulfuric acid to the residue and ignite. The weight of the residue should not exceed 0.0010 gram.

Chloride—Dissolve 1 gram in 15 cc. of warm water and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Phosphate—Dissolve 5 grams in 75 cc. of warm water, and add 10 cc. of nitric acid and 8 cc. of ammonium hydroxide. Warm to 60° C., add 50 cc. of ammonium molybdate solution, and shake for 5 minutes. Any precipitate should not be greater than is produced in a solution of equal volume with the same quantities of reagents and 0.05 mg. of PO_4.

Sulfate—Dissolve 4 grams in 75 cc. of hot water and add 1 cc. of hydrochloric acid. Heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and let stand overnight. Filter, wash and ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0010 gram greater than the weight of the ignited precipitate from a blank made with the quantities of the reagents used in the test, including filtration and ignition of the paper.

Arsenic—Dissolve 0.4 gram in 10 cc. of water and apply the modified Gutzeit test as described in the U. S. Pharmacopeia. The stain produced should correspond to not more than 0.002 mg. of arsenic.

Calcium—Dissolve 2 grams in 25 cc. of water and add 1 cc. of acetic acid and 5 cc. of 4 per cent ammonium oxalate solution. No turbidity should be observed in 10 minutes.

Heavy Metals—Dissolve 2 grams in 25 cc. of hot water and add 1 cc. of *N* hydrochloric acid. Heat to about 80° C. and add 5 cc. of hydrogen sulfide water. No darkening of the solution should be observed.

Iron—Add ammonium hydroxide to the solution tested for heavy metals until it is distinctly alkaline. Any greenish color should not be greater than is produced by 0.02 mg. of iron in an alkaline sulfide solution.

ACID FORMIC

Requirements

Assay—Not less than 87 per cent.
Dilution Test—To pass test.
Nonvolatile Matter—Not more than 0.002 per cent.
Acetic Acid—To pass test (limit about 0.4 per cent).
Chloride (Cl)—To pass test (limit about 0.001 per cent).
Sulfate (SO_4)—Not more than 0.002 per cent.
Sulfite (SO_3)—To pass test.
Heavy Metals—To pass test (limit about 0.0005 per cent lead; about 0.0005 per cent iron).

Tests

Assay—Titrate a weighed portion of the acid, after suitable dilution, with standard sodium hydroxide solution, using phenolphthalein indicator.

Dilution Test—Dilute 1 volume of the acid with 3 volumes of water. No turbidity should be observed within 1 hour.

Nonvolatile Matter—Evaporate 20 cc. to dryness on the steam bath and dry at 105° to 110° C. The weight of the residue should not exceed 0.0005 gram.

Acetic Acid—Dilute 1 cc. to 100 cc. Mix 10 cc. of this solution with 1.5 grams of yellow mercuric oxide. Heat on the steam bath for 20 minutes and then filter. The filtrate should not turn blue litmus paper in 30 seconds.

Chloride—Mix 4 cc. of the acid with 5 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride ion in an equal volume containing the quantities of reagents used in the test.

Sulfate—To 4 cc. add 0.01 gram of sodium carbonate and evaporate to dryness. Take up with 5 cc. of water, filter, and make up to a volume of 10 cc. Add 1 cc. of *N* hydrochloric acid and 1 cc. of 10 per cent barium chloride solution. Any turbidity, after 10 minutes, should not be greater than is produced in an equal volume of distilled water containing 0.01 gram of the same sodium carbonate, 1.2 cc. of *N* hydrochloric acid, 0.10 mg. of sulfate ion, and the volume of barium chloride used in the test.

Sulfite—Dilute 25 cc. of the acid with 25 cc. of water and add 0.1 cc. of 0.1 *N* iodine solution. The mixture should retain a distinct yellow color.

Heavy Metals—Dilute 5 cc. with 10 cc. of water, exactly neutralize with ammonium hydroxide, add 2 cc. of *N* hydrochloric acid, and pass hydrogen sulfide through the solution. The solution should not be darker than an equal volume of water containing 0.03 mg. of lead and 0.5 cc. of 0.1 *N* hydrochloric acid through which hydrogen sulfide has been passed. Add to the solution of the sample a slight excess of ammonium hydroxide. The solution should not be darker than an equal volume of water containing 0.03 mg. of iron and 0.5 cc. of 0.1 *N* hydrochloric acid and the quantities of hydrogen sulfide and ammonium hydroxide used in the test.

ACID SULFANILIC

Requirements

Residue on Ignition—Not more than 0.03 per cent.
Insoluble in Sodium Carbonate Solution—Not more than 0.02 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Nitrite (NO_2)—Not more than 0.00005 per cent.
Sulfate (SO_4)—Not more than 0.01 per cent.

Tests

Residue on Ignition—Ignite 3 grams in a platinum dish. The weight of the residue should not exceed 0.0010 gram.

Insoluble in Sodium Carbonate Solution—Dissolve 5 grams in 50 cc. of a clear 5 per cent solution of sodium carbonate (anhydrous), and let stand for 1 hour. If an insoluble residue remains, filter, wash with cold water, and dry at 105° C. The weight of the residue should not exceed 0.0010 gram.

Chloride—Boil 5 grams with 100 cc. of water until dissolved. Cool, dilute to 100 cc., mix well, and filter. To 10 cc. of the filtrate add 1 cc. of dilute nitric acid (1 + 2) and 1 cc. of approximately 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume containing the same quantities of reagents.

Nitrite—Add 0.5 gram to 50 cc. of water and add 5 cc. of sulfanilic 1-naphthylamine solution. Heat in a water bath with shaking until the sulfanilic acid is in solution. The solution should show no more pink color than a water blank containing 5 cc. of the reagent solution.

(The solution of sulfanilic 1-naphthylamine is made according to Griess-Ilosvay as follows: Dissolve 0.5 gram of acid sulfanilic in 150 cc. of 36 per cent acetic acid. Boil 0.1 gram of 1-naphthylamine with 20 cc. of water, pour off the colorless liquid from the residue, and add to 150 cc. of 36 per cent acetic acid. Mix the two solutions. If, on standing, the solution develops a pink color it may be discharged with a little zinc dust.)

Sulfate—Evaporate 60 cc. of the filtrate used in the test for chloride to about 15 cc., cool on ice, filter, and add to the filtrate 0.5 cc. of hydrochloric acid and 1 cc. of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.3 mg. of sulfate ion in an equal volume containing the same quantities of reagents.

ACID SULFUROUS

Requirements

Assay—Not less than 6 per cent of SO_2.
Nonvolatile Matter—Not more than 0.005 per cent.
Chloride (Cl)—Not more than 0.0005 per cent.
Arsenic (As)—Not more than 0.00005 per cent
Heavy Metals—To pass test (limit about 0.001 per cent lead).
Iron (Fe)—Not more than 0.0005 per cent.

Tests

Assay—Tare a glass-stoppered Erlenmeyer flask containing 50 cc. of 0.1 *N* iodine. Quickly introduce about 2 cc. of the acid, stopper, and weigh. Titrate the excess iodine with 0.1 *N* sodium thiosulfate solution.

Nonvolatile Matter—Evaporate 10 cc. to dryness, ignite at cherry redness for 5 minutes, cool, and weigh. The weight of the residue should not exceed 0.0005 gram.

Chloride—Digest 10 cc. with 2 cc. of nitric acid on the steam bath for 1 hour. Add 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.05 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Arsenic—Mix 5 cc. with 0.5 cc. of sulfuric acid and evaporate on the steam bath until free from sulfur dioxide and the volume has been reduced to about 2 cc. Dilute to about 5 cc. and determine the arsenic by the Gutzeit method as described in the U. S. Pharmacopeia.

Heavy Metals—Dilute 5 cc. with 10 cc. of water and boil to expel the sulfur dioxide. Neutralize to litmus with ammonium hydroxide, add 2 cc. of 0.1 *N* hydrochloric acid, dilute to 50 cc., and pass hydrogen sulfide gas through the solution. No darkening should be observed.

Iron—Evaporate 2 cc. to dryness. Treat the residue with 0.5 cc. of hydrochloric acid and 3 drops of nitric acid and re-evaporate. Take up with 2 cc. of hydrochloric acid, dilute to 20 cc., and add 3 cc. of 30 per cent ammonium thiocyanate solution. Any red color should not be greater than is produced by 0.01 mg. of iron under the same conditions.

ANILINE

Requirements

Color—Not more than a pale yellow.
Nonvolatile Matter—Not more than 0.005 per cent.
Hydrocarbons and Nitrobenzene—To pass test.
Boiling Range—183° to 186° C.

Tests

Nonvolatile Matter—Evaporate 10 cc., ignite, and weigh. The weight of the residue should not exceed 0.0005 gram.

Hydrocarbons and Nitrobenzene—Mix 5 cc. with 10 cc. of hydrochloric acid. The solution while still hot from the mixing should be clear and should remain clear after diluting with 15 cc. of cold water.

Boiling Range—When 100 cc. are distilled by the method described in the U. S. Pharmacopeia, not less than 95 cc. should distill within the temperature range indicated.

HYDROGEN PEROXIDE

Requirements

Strength—Not less than 28 per cent H_2O_2.
Nonvolatile Matter—Not more than 0.005 per cent.

Free Acid—Not more than 0.005 per cent as H_2SO_4.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrogen (N)—Not more than 0.001 per cent.
Phosphate (PO_4)—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.010 per cent.

Tests

Assay—Weigh about 1 cc. in a tared 100-cc. volumetric flask, fill to the mark with water, and mix thoroughly. To 20 cc. of this solution add 20 cc. of sulfuric acid (1 + 15) and titrate with 0.1 *N* potassium permanganate.

Nonvolatile Matter—Evaporate 10 cc. to dryness on the steam bath, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Free Acid—Dilute 10 cc. with 90 cc. of water free from carbon dioxide. Add 3 drops of 0.1 per cent methyl red solution and titrate with 0.02 *N* sodium hydroxide, making a correction for the alkali consumed by a blank containing 90 cc. of water free from carbon dioxide.

Chloride—Dilute 3 cc. with 15 cc. of water, add 1 cc. of 0.1 *N* silver nitrate, and add immediately 1 cc. of nitric acid. Any turbidity should not be greater than is produced by 0.03 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Nitrogen—Add a drop of sulfuric acid to 10 cc. and evaporate to about 2 cc. Transfer with the aid of water into a Kjeldahl flask. Add a solution of 0.1 gram of salicylic acid in 10 cc. of sulfuric acid and then about 0.2 gram of sulfur and 5 grams of potassium sulfate. Digest in the usual manner of a Kjeldahl nitrogen determination. Add 70 cc. of water and an excess of 40 per cent sodium hydroxide, distill the mixture until a volume of 50 cc. is obtained and Nesslerize one-half of the distillate. The color should not be greater than is produced by a blank containing a quantity of ammonium salt corresponding to 0.05 mg. of nitrogen.

Phosphate—Evaporate 10 cc. on the steam bath. Take up the residue with 10 cc. of nitric acid, dilute with 50 cc. of water, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake the solution (at about 40° C.) for 5 minutes, and allow to stand 0.5 hour. Any precipitate formed should be less than is produced when a quantity of an alkaline phosphate containing 0.05 mg. of phosphate (PO_4) is treated according to the above procedure. The ammonium molybdate solution is prepared as directed under the test for phosphate in ammonium nitrate (*3*).

Sulfate—Dilute 9 cc. to 100. To 5 cc. of the diluted sample add 5 cc. of water and 1 cc. of a solution containing in 100 cc. 10 grams of barium chloride ($BaCl_2.2H_2O$) and 5 cc. of hydrochloric acid. The turbidity should not be greater than is produced by 0.05 mg. of sulfate ion in a volume of 10 cc. to which has been added 1 cc. of the acid barium chloride solution.

MERCURIC BROMIDE

Requirements

Appearance—White or having at most a very faint yellow tinge. If a mercurous salt is present the product darkens on exposure to light.
Nonvolatile Matter—Not more than 0.020 per cent.
Insoluble in Methanol—Not more than 0.1 per cent.
Chloride (Cl)—To pass test (limit about 0.5 per cent).

Tests

Nonvolatile Matter—Ignite 2.5 grams with 1 cc. of sulfuric acid. The weight of the residue should not exceed 0.0005 gram.

Insoluble in Methanol—Dissolve 2 grams in 30 cc. of methanol. Filter on asbestos in a Gooch crucible, and wash with methanol until the washings remain unaffected by hydrogen sulfide. Dry at 105° to 110° C. The weight of the residue should not exceed 0.0020 gram.

Chloride—Weigh accurately about 0.7 gram and moisten with 5 cc. of water and 1 cc. of 36 per cent acetic acid. Add 5 grams of coarsely powdered zinc (20 to 30 mesh) and warm gently, shaking frequently until the supernatant liquid becomes clear (about 10 minutes). Filter, wash, and to the combined filtrate and washings add 2 cc. of ferric nitrate solution (about 8 per cent), 2 cc. of nitric acid, and 50 cc. of 0.1 *N* silver nitrate. Filter, wash, and titrate the excess silver nitrate with 0.1 *N* thiocyanate solution. The volume of silver nitrate consumed should correspond to not more than 55.9 cc. per gram of mercuric bromide.

POTASSIUM BIPHTHALATE

Requirements

Assay—Not less than 99.9 per cent.
Insoluble Matter—Not more than 0.005 per cent.
Loss at 100° C.—Not more than 0.05 per cent.
Chlorine Compounds (as Cl)—To pass test (limit about 0.003 per cent).
Sulfur Compounds (as S)—Not more than 0.002 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent as lead).
Iron (Fe)—Not more than 0.001 per cent.

Tests

Assay—Dry the sample for 1 hour at 120° C., and cool in a desiccator containing a good desiccant, such as concentrated sulfuric acid. Accurately weigh about 1 gram of the dried sample and transfer to a 300-cc. flask which has been swept free from carbon dioxide. Add 50 cc. of cool water that is free from carbon dioxide, stopper the flask, and shake gently until the sample is dissolved. When the sample is in solution, add 3 drops of a 1 per cent solution of phenolphthalein and titrate with an approximately 0.1 *N* solution of sodium hydroxide that is free from carbon dioxide, taking precautions to exclude the latter.

Determine the quantity of sodium hydroxide required to produce the end point by matching the color in another flask containing the indicator and the same volume of solution free from carbon dioxide. Subtract the amount required from that used in the first titration and calculate the acidity on the basis of the following equation:

$$KHC_8H_4O_4 + NaOH = KNaC_8H_4O_4 + H_2O$$

Each cubic centimeter of 0.1 *N* sodium hydroxide consumed corresponds to 0.02041 gram of $KHC_8H_4O_4$. (From U. S. Bureau of Standards Certificate of Analyses Sample No. 84, Washington, D. C., May 27, 1927.)

Insoluble Matter—Dissolve 10 grams in about 100 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash thoroughly, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Loss at 100° C.—Crush quickly a few grams and dry about 2 grams at 100° C. The loss in weight should not be greater than 0.0010 gram.

Chlorine Compounds—Mix 0.5 gram with 0.25 gram of sodium carbonate. Moisten the mixture and ignite until thoroughly charred, avoiding an unduly high temperature. Treat with 15 cc. of water and cautiously add 1 cc. of nitric acid. Filter, wash the residue with a few cubic centimeters of hot water, make to volume of 25 to 30 cc., and add 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.015 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Sulfur Compounds—Mix 2 grams with 1 gram of sodium carbonate and dissolve in water. Evaporate to dryness and char thoroughly with a flame free from sulfur. Treat with 25 cc. of water, add a few cubic centimeters of saturated bromine water, and heat on the steam bath for 15 minutes. Neutralize with hydrochloric acid, adding a slight excess of acid, boil gently to expel the bromine, filter, and wash. Add to the filtrate, which should measure about 25 cc., 2 cc. of 10 per cent barium chloride solution. Any turbidity should not be greater than is produced by 0.12 mg. of sulfate ion in an equal volume with the quantities of reagents used in the test.

Heavy Metals—Dissolve 1.75 grams in 15 cc. of hot water and exactly neutralize the solution with ammonium hydroxide. Dissolve in this same solution 0.25 gram more of potassium biphthalate and add 10 cc. of hydrogen sulfide water. No darkening of the solution should be observed.

Iron—To the solution tested for heavy metals add ammonium hydroxide until it is alkaline to litmus. Any greenish color should not be greater than is produced by 0.02 mg. of iron in an alkaline sulfide solution.

POTASSIUM OXALATE

Requirements

Insoluble Matter—Not more than 0.010 per cent.
Neutrality—To pass test (limit of alkalinity equivalent to 0.10 per cent K_2CO_3, limit of acidity equivalent to 0.05 per cent KHC_2O_4).
Chloride (Cl)—Not more than 0.002 per cent.
Sulfate (SO_4)—Not more than 0.010 per cent.
Ammonia (NH_3)—Not more than 0.002 per cent.
Heavy Metals—To pass test (limit about 0.002 per cent lead).
Iron (Fe)—To pass test (limit about 0.001 per cent).
Sodium (Na)—To pass test (limit about 0.02 per cent).
Substances Darkened by Hot Sulfuric Acid—To pass test.

Tests

Insoluble Matter—Dissolve 10 grams in 100 cc. of water and allow to stand on the steam bath for 1 hour. Filter on asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0010 gram.

Neutrality—Dissolve 2 grams in 150 cc. of water free from carbon dioxide. Add 0.2 cc. of phenolphthalein solution and boil the solution in a flask of resistant glass for 10 minutes while passing through it a current of air free from carbon dioxide. Prepare a color standard by adding 0.2 cc. of phenolphthalein solution to 150 cc. of carbon dioxide-free water containing 10 cc. of 0.1 *N* sodium hydroxide solution, and diluting 6 cc. of this red liquid to 100 cc. with carbon dioxide-free water. Titrate the potassium oxalate solution with 0.01 *N* acid or alkali as required to bring its color to match that of the prepared standard. Not more than 1.4 cc. of the 0.01 *N* acid or 0.8 cc. of 0.01 *N* alkali solution should be required.

Chloride—Ignite 2.5 grams to carbonate. Dissolve in 50 cc. of water, neutralize with nitric acid, and filter if necessary. Make up to 100 cc. To 10 cc. in a test tube, add 1 cc. of dilute nitric acid (1 + 9) and 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity should not be greater than is produced by 0.005 mg. of chloride ion in 10 cc. of distilled water to which are added the quantities of acid and silver nitrate used in the test.

Sulfate—Ignite 4 grams in a platinum crucible, using a sulfur-free flame. Dissolve the residue in 50 cc. of water, neutralize with hydrochloric acid, and add an excess of 1 cc. of *N* hydrochloric acid. Dilute to about 100 cc., heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand for 18 hours. Any precipitate formed should not weigh after ignition over 0.0010 gram more than the precipitate obtained in a blank test made with the same quantities of reagents and including filtration and ignition of the paper.

Ammonia—Dissolve 1 gram in 20 cc. of water, and add 2 cc. of Nessler's solution. The color should not be more than is produced by a quantity of ammonium salt corresponding to 0.02 mg. of NH_3 in an equal volume of solution containing the quantity of Nessler's solution used in the test.

Heavy Metals—Ignite 2 grams to carbonate and dissolve the residue in 10 cc. of water. Neutralize with hydrochloric acid and add an excess of 1 cc. of 0.1 *N* hydrochloric acid. Dilute to 25 cc. with water and pass hydrogen sulfide through the diluted solution. Any brown color should not be darker than is produced by 0.04 mg. of lead under the same conditions.

Iron—Ignite 3 grams to carbonate and dissolve the residue in 20 cc. of water. Neutralize with hydrochloric acid and add an excess of 1 cc. of strong acid. Add 1 drop of bromine and boil until nearly all color is gone. After the solution has cooled to room temperature dilute to 25 cc., add 2 cc. of hydrochloric acid, and 3 cc. of 30 per cent ammonium thiocyanate solution. The color should not be more than is produced in a control test made with 0.03 mg. of iron.

Sodium—Ignite 1 gram to carbonate in a platinum crucible and dissolve the residue in 5 cc. of dilute hydrochloric acid. Test the solution on a platinum wire in the flame. No pronounced yellow color should be produced.

Substance Darkened by Hot Sulfuric Acid—Heat 1 gram in a recently ignited test tube with 10 cc. of sulfuric acid until the appearance of fumes. The acid should not acquire more than a slight brownish tinge.

SODIUM SULFITE ANHYDROUS

Requirements

Assay—Not less than 95 per cent Na_2SO_3.

Insoluble Matter—Not more than 0.01 per cent.

Free Acid—To pass test.

Free Alkali—To pass test (limit of alkalinity equivalent to 0.3 per cent Na_2CO_3).

Chloride (Cl)—Not more than 0.02 per cent.

Arsenic (As)—Not more than 0.0002 per cent.

Heavy Metals—Not more than 0.002 per cent as lead.

Iron (Fe)—Not more than 0.001 per cent.

Tests

Assay—Weigh accurately about 0.25 gram and add it to 50 cc. of 0.1 *N* iodine solution (the sulfite must be added to the iodine solution). After standing 5 minutes add 1 cc. of hydrochloric acid and titrate the excess iodine with 0.1 *N* thiosulfate.

Insoluble Matter—Dissolve 10 grams in 100 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Free Acid—Dissolve 1 gram in 10 cc. of water and add 2 drops of phenolphthalein solution. A pink color should be produced.

Free Alkali—Dissolve 1 gram in 10 cc. of water and add 1.5 cc. of 30 per cent hydrogen peroxide which has been previously neutralized to methyl red. Shake well and let stand for 5 minutes. Titrate with 0.1 *N* acid, using methyl red indicator. Not more than 0.6 cc. of the 0.1 *N* acid should be required to neutralize the solution.

Chloride—Dissolve 1 gram in 10 cc. of water, add 1.5 cc. of 30 per cent hydrogen peroxide, and dilute to 100 cc.; take 10 cc., dilute to 20 cc., and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution containing the same quantities of nitric acid and silver nitrate used in the test. It is not necessary to add hydrogen peroxide to the blank.

Arsenic—Dissolve 1 gram in 10 cc. of water, add 1 cc. of sulfuric acid, evaporate to about 1 cc. on the steam bath, and apply to the residue the modified Gutzeit test as described in the U. S. Pharmacopeia.

Heavy Metals—Dissolve 2 grams in 10 cc. of water, add 5 cc. of hydrochloric acid, and evaporate to complete dryness on the steam bath. Take up residue in 1 cc. of 0.1 *N* hydrochloric acid and 25 cc. of water and pass in hydrogen sulfide. Any darkening should not be greater than is produced in a control test made with a quantity of lead salt equivalent to 0.04 mg. of lead and including evaporation of 5 cc. of hydrochloric acid.

Iron—Decompose 1 gram with 2 cc. of hydrochloric acid and evaporate to dryness. Take up the residue in 2 cc. of water followed by 2 cc. of hydrochloric acid and 20 cc. of water, add 3 drops of bromine water, boil off the bromine, cool, and add 3 cc. of 30 per cent ammonium thiocyanate solution. Any red color produced should not be greater than is produced in a control test made with 0.01 mg. of iron.

CORRECTIONS FOR PUBLISHED SPECIFICATIONS

Replace or modify requirements and tests previously printed as indicated below:

ACID PHOSPHORIC (*4*)

Test

Assay—After last sentence add, "One cubic centimeter of normal alkali solution corresponds to 0.049 gram of H_3PO_4."

AMMONIUM SULFATE (*2*)

Requirement

Nonvolatile Matter—Not more than 0.015 per cent.

CALCIUM CHLORIDE ($CaCl_2.2H_2O$) (*7*)

Requirement

Insoluble and Ammonium Hydroxide Precipitate—Not more than 0.015 per cent.

Test

Assay—Second sentence should read, "Transfer 25 cc. to a 200-cc. graduated flask . . . ."

SODIUM BISMUTHATE (*3*)

Requirement

Chloride—Not more than 0.002 per cent.

Test

Chloride—Make comparison with 0.02 mg. of chloride.

Specifications Previously Published

(1) Committee on Analytical Reagents, Ind. Eng. Chem., **17**, 756 (1925).
(2) *Ibid.*, **18**, 636, 759 (1926).
(3) *Ibid.*, **19**, 645 (1927).
(4) *Ibid.*, **19**, 1369 (1927).
(5) *Ibid.*, **20**, 979 (1928).
(6) *Ibid.*, Anal. Ed., **1**, 171 (1929).
(7) *Ibid.*, **2**, 351 (1930).
(8) *Ibid.*, **3**, 221 (1931).
(9) *Ibid.*, **4**, 154 (1932).
(10) *Ibid.*, **4**, 347 (1932).

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Photometric Investigation of Nessler Reaction and Witting Method for Determination of Ammonia in Sea Water

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Four Nessler reagents have been prepared and the color developed by them at low ammonia concentrations in distilled water and in sea water has been investigated photometrically.

In distilled water, all four reagents give a definite nonsensitive region, varying between 0.00 to 0.03 and 0.00 to 0.08 mg.

Treadwell's reagent, in sea water, does not have a nonsensitive region. It is therefore possible to determine as little as 0.003 mg. of ammonia nitrogen in sea water without resorting to the artifice of adding known amounts of nitrogen. The sensitivity of the Treadwell reagent increases with increasing chlorinity. With the Treadwell reagent it has been shown that Beer's law does not apply for concentrations of ammonia nitrogen less than 0.02 mg. per liter.

There is no error due to adsorption in the Witting method for the determination of ammonia in sea water.

BUCH (*3*), in his spectrophotometric studies of the Witting method for the determination of free ammonia in ocean water, found that the Nessler reagents were insensitive to concentrations less than 0.05 mg. nitrogen per liter (in distilled water). It was therefore deemed necessary to add a known quantity of ammonia if a lesser amount was originally present. Urbach (*7*) also has made a photometric investigation of the Nessler reagent in distilled water and like Buch found that Beer's law holds, but did not try concentrations less than 0.2 mg. per liter—the region of greatest interest to the oceanographer. Wattenberg (*8*), using his direct nesslerization method, did not find this minimum sensitivity in sea water and was able to estimate 0.005 mg. or less of ammonia nitrogen per liter. Cooper (*4*) with Wattenberg's method but a modified reagent was able to distinguish visually between 0.000 and 0.003 mg. The authors (*5*) using an entirely different reagent were unable to determine less than 0.02 mg.

It was believed that the inconsistent results previously mentioned were due to the varying sensitivities of the Nessler reagents employed, and in the Witting method to partial adsorption of ammonia during the precipitation of the interfering ions. If adsorption does take place, the Witting method is useless. This is of importance, as this method is otherwise the better for the determination of ammonia in sea water having a large plankton content. Plankton, which is believed to cause a turbidity in the sea water standards of the Wattenberg method, is removed in the Witting procedure by occlusion in the precipitate of barium sulfate, calcium carbonate, and magnesium hydroxide.

APPARATUS

The Zeiss Pulfrich (gradation) photometer was used. In order to obtain significant variation in light absorption in the small range of ammonia concentrations studied, photometer tubes approximately 30 cm. long and 2.5 cm. in diameter were constructed. The per cent light transmitted by the nesslerized ammonia solutions as compared with distilled water is read directly on the instrument. Distilled water is preferable as a reference standard since it is affected less by light and oxygen than a standard made of ammonia-free water plus Nessler reagent as used by Urbach. Since the light absorption of the Nessler color is in the violet end of the spectrum, as Urbach has shown, the S-43 filter provided with the instrument was used. This filter has an effective range of 200 to 250 $\mu\mu$ and transmits light with an average wave length of 430 $\mu\mu$. The general form of the curves was verified by means of the S-47 filter, which has an average wave length of 470 $\mu\mu$. The tubes containing the ammonia and distilled water solutions were always interchanged to avoid errors owing to unequal illumination of the two sides of the photometer. Each reading was checked by another observer so that at least four readings were averaged for each sample reported in the various figures.

REAGENTS AND SOLUTIONS

Nessler reagents were made according to the directions given by (*A*) Ringer and Klingen; (*B*) Raben; (*C*) Standard Methods of Water Analysis; and (*D*) Treadwell. All

chemicals were freed of ammonia, and ammonia-free water was used at all times.

Ringer and Klingen (*3*). Add slowly 35 grams of potassium iodide in 100 ml. of water to 16 grams of mercuric chloride in 300 ml. of water until a permanent precipitate remains. Add slowly 200 grams of potassium hydroxide in 600 ml. of water to the above solution.

Raben (*3*). Add 50 grams of potassium iodide in 50 ml. of boiling water to a boiling solution of 25 grams of mercuric chloride in 300 ml. of water. Filter the cooled solution into 300 ml. of water containing 150 grams of potassium hydroxide, and then dilute to a liter.

Standard Methods of Water Analysis (*1*). To 50 grams of potassium iodide in 35 ml. of cold water add a saturated mercuric chloride solution until a slight precipitate persists. Add 400 ml. of 9 *N* potassium hydroxide and dilute to one liter.

Treadwell (*6*). Dissolve 115 grams of mercuric iodide and 80 grams of potassium iodide in enough water to make 500 ml. Add 500 ml. of 6 *N* sodium hydroxide.

The concentrations are compared in the following table:

Table I. Concentrations of Various Nessler Reagents

Reagent	Concentration Hg (as K_2HgI_4?)	Hydroxide Concentration
Ringer and Klingen	0.059 *M*	3.6 *N*
Raben	0.092 *M*	2.7 *N*
Standard Methods	0.09 *M* (approx.)	3.6 *N*
Treadwell	0.25 *M*	3.0 *N*

These reagents were selected because they have all been used in the determination of ammonia in sea water. The reagent of Urbach gives approximately the same concentration as Raben's when 1 ml. is used per 100 ml. of water instead of 2 ml. per 100 ml., as is usual with the other reagents. Wattenberg (*9*) suggests the use of a Nessler reagent (attributed by him to Treadwell) which is approximately 5 *N* in sodium hydroxide and 0.2 *M* in mercury. The authors were unable to prepare such a reagent, as a copious precipitate was obtained when alkali was added.

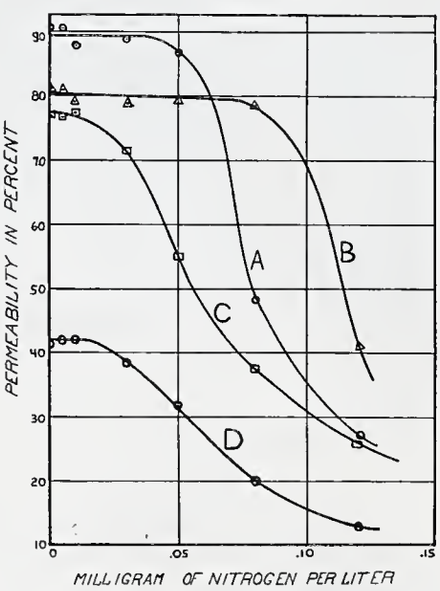

Figure 1. Sensitivity of Nessler Reagents (*A*, Ringer and Klingen; *B*, Raben; *C*, Standard Methods; *D*, Treadwell) in Distilled Water Using "S-43" Filter

The barium chloride (200 grams of barium chloride–dihydrate per liter) and sodium hydroxide–sodium bicarbonate (200 grams of sodium hydroxide and 69 grams of sodium bicarbonate per liter) solutions were freed of ammonia by partial evaporation. Ammonia-free sea water was prepared by adding half a volume of distilled water to sea water and evaporating to the original volume. From this the desired chlorinities were obtained, either by further evaporation or dilution as the case might be.

Light Absorption by Nessler Color in Distilled Water

The variation of light absorption in distilled water with varying ammonia content was first determined one hour after nesslerization for each of the four Nessler reagents (Figure 1). Time of color development was also determined for a concentration of 0.1 mg. ammonia nitrogen per liter (Table II).

Table II. Time of Development of Nessler Color in Distilled Water Containing 0.1 mg. Ammonia Nitrogen per Liter

Reagent	Permeability in Per Cent after: (Time in hours) 0	0.5	1	2	26	34	50
Ringer and Klingen	94.0	84.0	44.0	32.3	23.0	24.5	22.2
Raben	91.0	86.0	83.0	79.0	33.0	30.0	25.5
Standard Methods	40.0	29.0	29.0	27.0	26.0	23.5	22.0
Treadwell	34.0	17.5	17.0	16.0	17.2	17.5	18.0

The Treadwell and Standard Methods reagents showed practically complete color development at the end of 30 minutes, whereas the development was complete only after 5 and 10 hours in the case of the Ringer and Klingen, and Raben reagents, respectively. The color intensity was unchanged for 50 hours, but was exposed to the photometer light only during readings. Urbach found that color started to fade after 30 minutes, but his samples were illuminated continuously.

It might be thought that all four Nessler reagents would give the same curve if sufficient time were allowed for complete color development. This was not the case. After 24 hours the form of the curves remained unchanged, while the nonsensitive region was reduced by only 0.01 mg. in the case of the Ringer and Klingen and Raben reagents.

It was thought desirable to compare these results with those in sea water which had been diluted with the Witting reagents. To accomplish this the amount of ammonia actually present in the distilled water was only $^{25}/_{28}$ of that indicated on the graph.

Accuracy of Witting Method

To 500 ml. samples of ammonia-free sea water (Cl = 14.4 parts per thousand) 0.000, 0.0025, 0.005, 0.015, 0.025, 0.04, and 0.06 mg. of nitrogen as ammonia was added, the sample well shaken, and the interfering ions precipitated with 16 ml. of barium chloride solution and 32 ml. of sodium hydroxide–sodium bicarbonate. After standing one week, the clear supernatant liquid was siphoned, and 125 ml. portions were nesslerized with 2.5 ml. of reagent (Standard Methods and Treadwell). The color intensity was evaluated by means of the photometer after 30 minutes.

A 3500-ml. sample of the same water was treated with proportionate amounts of barium chloride and sodium hyhydride–sodium bicarbonate solutions. The clear liquid was siphoned and sufficient ammonia added to 125-ml. portions to give the same concentrations as above. The permeabilities are given in Figure 2.

Attempts were made to speed the settling of the precipitate by centrifugalizing, since it is desirable to analyze the samples immediately, but turbidities were always obtained upon nesslerization. Evidently the precipitation is complete only on standing for several days.

If I is the value of the scale reading (permeability in per cent) and I_0 is the value of I corresponding to zero ammonia concentration, then $-\log I/I_0$ plotted against the ammonia content should give a straight line if Beer's law holds for these dilutions. This has been done in Figure 3 for the Treadwell reagent, in distilled water, and sea water of chlorinities 10.0, 14.4, and 18.0 parts per thousand. The plotted values for sea water were those obtained after first precipitating with barium chloride and sodium hydroxide–

sodium bicarbonate solutions and then adding known quantities of ammonia.

To determine the ammonia content of sea water, the following procedure was used:

To 250 ml. of the sample in a 300-ml. bottle add in succession 10 ml. of barium chloride solution and 20 ml. of sodium hydroxide–sodium bicarbonate, shaking after each addition. With chlorinities less than 17 parts per thousand, smaller quantities of reagents were used (Cl = less than 11.0 parts per thousand, 5 ml. $BaCl_2$; Cl = 11.0–13.9 parts per thousand, 6.5 ml. $BaCl_2$; Cl = 14.0–16.9 parts per thousand, 8.0 ml. $BaCl_2$, with twice as much NaOH–

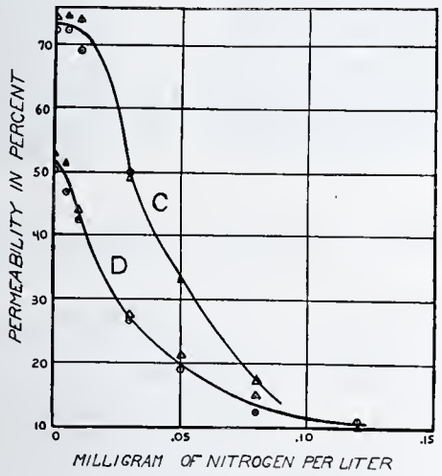

Figure 2. Accuracy of Witting Method in Sea Water Using "S-43" Filter (*C*, Standard Methods Reagent; *D*, Treadwell Reagent)

△ Precipitated before addition of NH_3
⊙ Precipitated after addition of NH_3

$NaHCO_3$ in each case). This eliminated difficulties encountered in obtaining clear solutions on nesslerization, which were believed to be due to too great an excess of reagents. After standing for at least 3 days, the supernatant liquid was siphoned and the ammonia determined photometrically.

This procedure was tested on eighteen samples taken in Hood Canal, April 29 to 30, 1933, and gave excellent results in every case. Three duplicates, which were allowed to stand for 25 days, showed 0.010 mg. more ammonia nitrogen than those tested after 10 days, indicating a probable decomposition of organic matter in the alkaline solution. This would be the greatest increase normally expected, since these samples were especially rich in plankton. The necessity of finishing the determination as soon as possible after sampling is, however, evident.

Discussion

It is apparent from Figure 1 that the various Nessler reagents have different characteristics at low ammonia concentrations, but uniformly show a minimum sensitivity. The form of the curve depends apparently on the concentration of the constituents in the reagent. As far as results in distilled water are concerned, the Standard Methods reagent is preferable, since it has a shorter nonsensitive region. The Treadwell reagent has too great a color of its own, and in addition, samples nesslerized with it always give a precipitate of mercuric iodide on standing. In sea water, however, the Treadwell reagent gives far better results. In the chlorinities investigated no limiting sensitivity was apparent, but there was a very definite change in the log curve (Figure 3) at N = 0.02 mg. per liter in every case. In addition, the sensitivity of the reagent apparently increases with increasing chlorinity.

The Standard Methods reagent shows a definite but shorter nonsensitive region in sea water, but its use is excluded by a turbidity which always appears at ammonia concentrations of 0.1 mg. nitrogen per liter or higher, which is not the case with the Treadwell reagent. The Ringer and Klingen and Raben reagents are not applicable, as they develop their color too slowly, usually give a turbidity, and have large nonsensitive regions in sea water as well as in distilled water.

Two Nessler reagents which had been prepared for 19 months were also tested, one of which, the Treadwell reagent, was much less sensitive and dependable in distilled water, but gave satisfactory results in sea water. The other, a Standard Methods reagent, was slightly more sensitive (distilled water) after standing, but was not tested in sea water.

The above Standard Methods reagent was the one used by the authors (*5*) in the determination of ammonia in sea water by the Wattenberg method. As the minimum sensitivity for this reagent is 0.02 mg. of nitrogen per liter, the inability of the authors to detect less than this quantity is thus explained. Moreover, it should be noted that this minimum sensitivity likewise applies to the determination of Kjeldahl and albuminoid nitrogen in water so that a zero blank does not necessarily mean there is no ammonia, but merely that 0.02 mg. or less of nitrogen per liter is present.

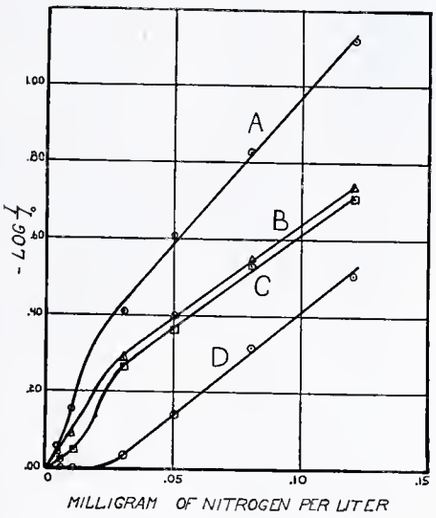

Figure 3. Applicability of Beer's Law to Nessler Reaction Using Treadwell Reagent and Small Concentrations of Ammonia in Distilled Water (*D*) and Sea Water of Varying Chlorinity (*C* = 10, *B* = 14.4, *A* = 18 Parts Cl per Thousand)

Figure 2 shows that there is no significant adsorption of ammonia on the precipitate, as in most cases the values by the two methods agree within 0.005 mg. The Witting method can therefore be used in sea water with little error arising from this source. Furthermore, it is possible to obtain an accurate standard curve by addition of known quantities of ammonia to sea water from which the interfering ions have previously been removed. Figure 2 also shows that, with the Treadwell reagent, it is possible to determine directly as little as 0.003 mg. of ammonia nitrogen per liter without resort to the artifice of adding 0.05 mg. of nitrogen to each sample.

It has been observed by the authors, and also by Braarud and Klem (*2*) that artificial ammonia-free sea water as prepared in the above experiments gives a slight color with the Nessler reagent which is not obtained with naturally occurring ammonia-free water. Where possible, therefore, it is desirable to make standards from untreated ammonia-

free sea water, which in the Puget Sound region is most apt to be found in the surface waters.

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X-Ray Method for Quantitative Comparison of Crystallite Orientation in Cellulose Fibers

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The relation between orientation of the crystallites or micelles and various properties of cellulose fibers is pointed out and an x-ray method for quantitatively comparing the orientation is described. The method is based upon the assumption that the distribution of the crystallites around the pencil of x-rays is proportional to the distribution of intensity around the 002 diffraction ring. Intensity measurements are made with a microdensitometer equipped with a rotating stage.

The distribution of the crystallites is calculated from the intensity values and the orientation is expressed by distribution curves which may be differentiated from one another by statistical methods. The data obtained may be used to study the structure of the fiber or to predict physical and chemical properties which are anisotropic. Typical data for three grades of cotton are presented to show the sensitiveness of the method.

That the orientation of the cellulose structural units varies widely in different fibers and in the same fiber (*1*, *8*) is well known, and its influence upon the physical and chemical properties of the fiber has been discussed by many investigators (*15*, *23*), particularly with reference to the degree of mercerization, tensile strength, classification, elasticity, and dyeing properties of cotton (*5*, *6*, *19*, *31*); the swelling, elasticity, tensile strength, ability to take dyes, resistance to enzymatic decomposition, gloss, creasing resistance, refractive index, and extension of rayon (*3*, *5*, *7*, *9*, *11*, *18*, *19*, *21*, *22*, *28*); and the density, tensile strength, expansion, and shrinkage of wood (*1*, *17*, *32*).

The use of x-rays in studying this orientation and differentiating between the various textile fibers, especially rayon, has been described by Clark (*5*), Mark (*20*), and others. These investigators, however, used a visual method of comparing the x-ray patterns which is essentially qualitative in nature. It is the purpose of this paper to describe briefly an improvement over the visual method, which enables a quantitative comparison to be made, and to point out the possible applications of the method.

The improved method is based on a comparison, for different samples, of the relative intensity distribution along the circle on which the 002 interference maxima are localized. Although the significance of cellulose fiber diagrams has been developed by Polanyi and Weissenberg (*26*, *27*) and the relation between crystal orientation and sharpness of the localized maxima is explained in textbooks on x-rays (*2*, *4*), the basis of the method may be explained briefly as follows:

Figure 1 shows typical x-ray patterns of a cellulose sheet and a bundle of ramie fibers. In both patterns the most intense interference (A_3 line) is due to the 002 planes (*24*). Since these planes are parallel to the long axis of the crystallites (*24*, *35*), each plane at angle θ to the x-ray beam (fulfilling the conditions of the Bragg equation $n\lambda = 2d \sin \theta$) will diffract x-rays in the limiting case, upon the 002 diffraction ring at right angles to the long axis of the crystallite. The diffraction ring registered on the photographic film is thus a summation of the individual diffractions from all the diffracting crystallites, and a comparison of the intensity distribution around this ring gives a measure of the distribution of the crystallites around the pencil of x-rays. For a complete picture of the orientation in any sample it is necessary to obtain an x-ray pattern with the sample inclined at various angles to the x-ray beam. However, for comparing the orientation of different fibers, one pattern taken with the x-ray beam perpendicular to the fiber axis is sufficient. A perfectly uniformly intense 002 diffraction ring, such as that obtained with the x-ray beam perpendicular to the cellulose sheet, implies that the long axes of the crystallites have a random orientation in the plane of the sheet. If the intensity is concentrated into localized maxima, as is the case for the x-ray beam perpendicular to the ramie fibers, then the crystallites approach a parallel arrangement along the fiber axis.

Experimental

The intensity measurements are made on a microdensitometer of the "photograph wedge" type, the principle of which was first described by Hartman (*14*) and more recently by Vasil'ev (*36*). It is manufactured by the Gaertner Scientific Corporation and involves some novel features. The wedge used is not strictly a photographic wedge but a dyed gelatin wedge between glass plates. This is essential in order to give the necessary linear relation between density and scale readings. To make up for the lack of grain of this type wedge a

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grain plate is placed at the focus of the comparison microscope which makes it unnecessary to defocus the microscope viewing the spectrum line. The shifting of the cube which was present in the original Hartman microdensitometer has been eliminated by utilizing a short vertical slit at the silvered horizontal strip of the dividing surface. The readings, which are read from a scale dividing arbitary units from 0 to

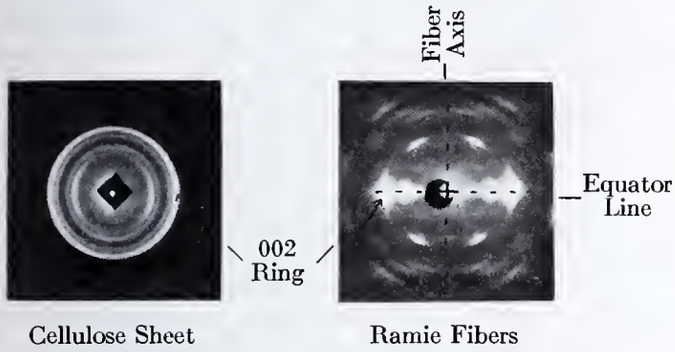

FIGURE 1. X-RAY PATTERN ILLUSTRATING RANDOM AND PREFERRED ORIENTATION

100, are proportional to the densities and consequently to the logarithm of the reciprocal of that portion of the light transmitted. The wedge type is more satisfactory than the registering type of microphotometer (*12, 13, 33*), since it gives definite, duplicable values for the intensity which may be used as the basis of calculations. A special calibrated rotating stage was constructed which allows the film to be rotated through 360° with the microdensitometer focused on the 002 line. The area included in the measurement is about 0.05 mm. wide and 0.8 mm. long, the long dimension being across the diffraction ring and including about one-half to two-thirds the width of the ring. The position of the film in focus may be read directly from the stage. Figure 2 shows the microdensitometer equipped with the rotating stage.

Although the planes which are parallel to the fiber axis diffract on the "equator line," at right angles to the fiber, the equator line will be referred to as the 0° position in order to avoid confusion in this discussion. Readings may be made every 2°, 5°, or 10°, depending upon the accuracy desired.

FIGURE 2. MICRODENSITOMETER EQUIPPED WITH ROTATING STAGE

Readings every 5° are satisfactory for most purposes and the number of these made in each quadrant will depend also upon the accuracy desired. In order to eliminate errors due to failure to mount the film and sample perpendicular to the x-ray beam, uneven scattering, or the slightly off-center position of the film on the stage, readings should be made over a 360° range in every case. A typical data sheet is shown in Table I.

In this table, and also in data given elsewhere, the angles ending in 0 are read in two quadrants and those ending in 5 in opposite quadrants. This gives two readings every 5° which

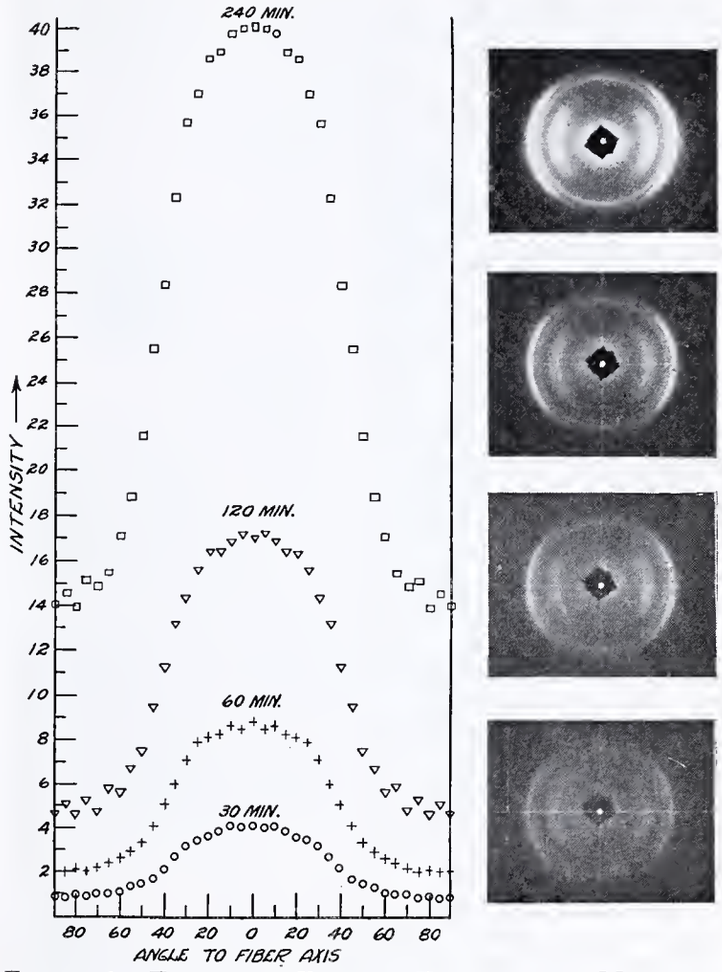

FIGURE 3. EFFECT OF TIME OF EXPOSURE ON MEASURED INTENSITY CURVES

(X-ray photographs represent times of exposure corresponding to curves)

are averaged. If more accurate data are desired four readings for each 5° angle should be averaged.

TABLE I. TYPICAL DATA SHEET

Sample 351 (cotton)

Angle	Readings (Quadrant) 1	2	3	4	Average	Corrected	%
0	42.6	42.0	..	..	42.3	34.0	12.00
5	..	..	41.8	41.8	41.8	33.5	11.90
10	41.4	41.4	..	..	41.4	33.1	11.70
15	..	..	40.2	41.0	40.6	32.3	11.40
20	38.0	38.6	..	..	38.3	30.0	10.60
25	..	..	35.6	36.4	36.0	27.7	9.80
30	30.0	30.6	..	..	30.3	22.0	7.80
35	..	..	27.5	28.6	27.0	18.7	6.63
40	21.6	21.6	..	..	21.6	13.3	4.71
45	..	..	18.2	19.0	18.6	10.3	3.65
50	15.2	13.8	..	..	14.5	6.2	2.20
55	..	..	13.6	13.2	13.3	5.0	1.77
60	11.6	12.2	..	..	11.9	3.6	1.27
65	..	..	11.0	11.6	11.3	2.9	1.03
70	10.2	10.4	..	..	10.2	1.9	0.67
75	..	..	11.2	11.0	11.1	2.8	0.99
80	10.4	9.6	..	..	10.1	1.7	0.60
85	..	..	9.6	10.2	9.9	1.6	0.57
90	10.0	10.0	..	..	10.0	1.7	0.60
					Total	282.3	

$$\text{Correction} = \frac{8.5 + 8.0 + 8.5 + 8.2}{4} = 8.3$$

A correction for the scattered radiation must be subtracted from the average reading, and this may be obtained by reading the intensity on the lightest portion of the film between the 002 line and the next line of larger diameter for each quadrant and taking the average as the correction factor. The corrected readings are then converted to a percentage basis. Representing the data on a percentage basis eliminates the necessity of carefully controlling such experimental variables as time of exposure, intensity of the x-ray beam, thickness of sample, as well as the temperature and time of developing. These factors, however, should be held constant for accurate work.

Several experimental factors must be controlled. For example, the fiber axis of the sample and a flat photographic plate should be perpendicular to a small parallel pencil of x-rays. Best results are obtained with filtered copper radiation and a sample to film distance of 5 cm. The photographic plate must be carefully shielded from outside scattered radiation. The fibers should be arranged symmetrically in the path of the x-ray beam, and in photographing fibers such as cotton, it is imperative that they be arranged in a parallel condition. A special apparatus for preparing specimens of cotton meeting these requirements has been constructed and will be described elsewhere in connection with the application of this method to cotton fibers. The center of the diffraction rings and the 90° and 0° positions of the film should coincide with the corresponding positions on the rotating stage. If this condition is fulfilled, readings made at equal angles on both sides of the 0° position will be identical.

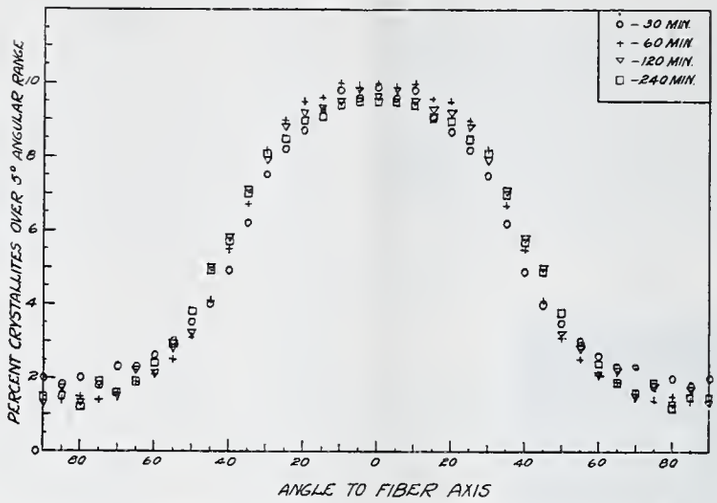

Figure 4. Effect of Time of Exposure on Measured Intensity Curves

(Same data as Figure 3 corrected to percentage basis)

Interpretation of Curves

So far, readings have been obtained which give intensity distribution curves. Before these curves can be defined or interpreted in terms of crystallite orientation they must be put on a strictly comparable basis. This is accomplished by converting the observed intensity values to relative or percentage values by dividing each reading by the total and multiplying by 100. Each curve plotted from these values has a constant area and the height of the curve at any angle to the fiber axis is proportional to the relative number of crystallites at that angle. The value at each point on the curve is designated as the relative per cent of the total crystallites over a 5° angular range at that point. The curves may be designated as an "empirical measuring stick" by which the relative orientation of different fibers may be compared. For example, examination of the data in Table I shows that about 9.8 per cent of the crystallites for that sample are orientated between 22.5° and 27.5° to the fiber axis. This is not an absolute value, but a relative value which may be compared with that obtained from another sample. Plotting the data to the scale of 10° = 1 per cent gives standard curves which may be compared directly. How the measured intensity curves are transposed to relative intensity curves and plotted in terms of crystallite orientation is illustrated in Figures 3 and 4. Figure 3 shows observed intensity values for 0.5, 1, 2, and 4-hour exposures of the same material. Figure 4 shows the same data after being corrected to a

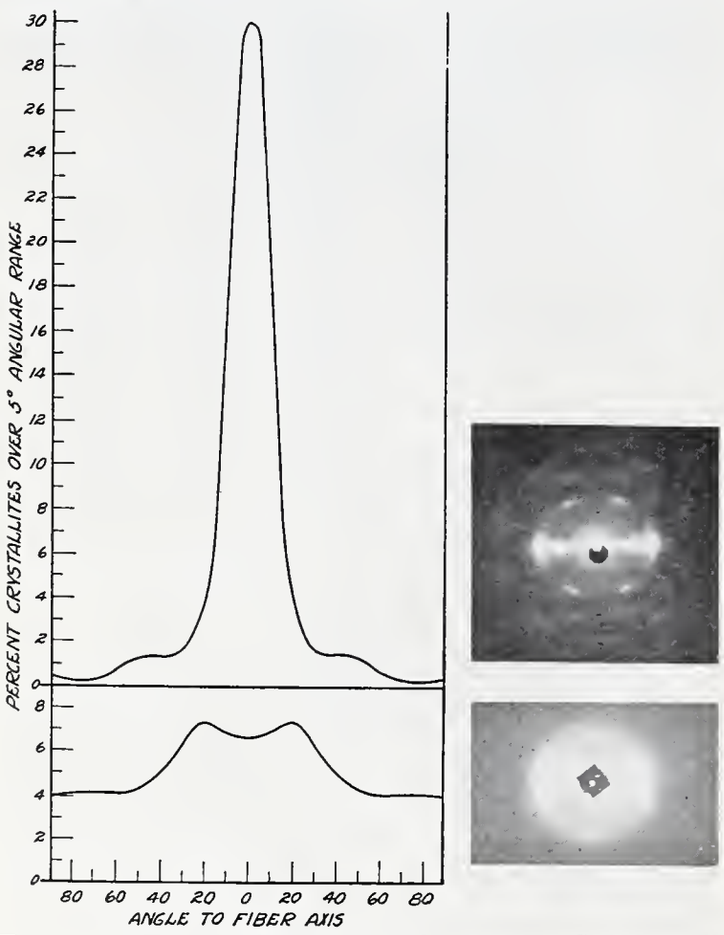

Figure 5. Typical Orientation Curves for Compression Wood and Ramie

(Upper, ramie. Lower, compression wood)

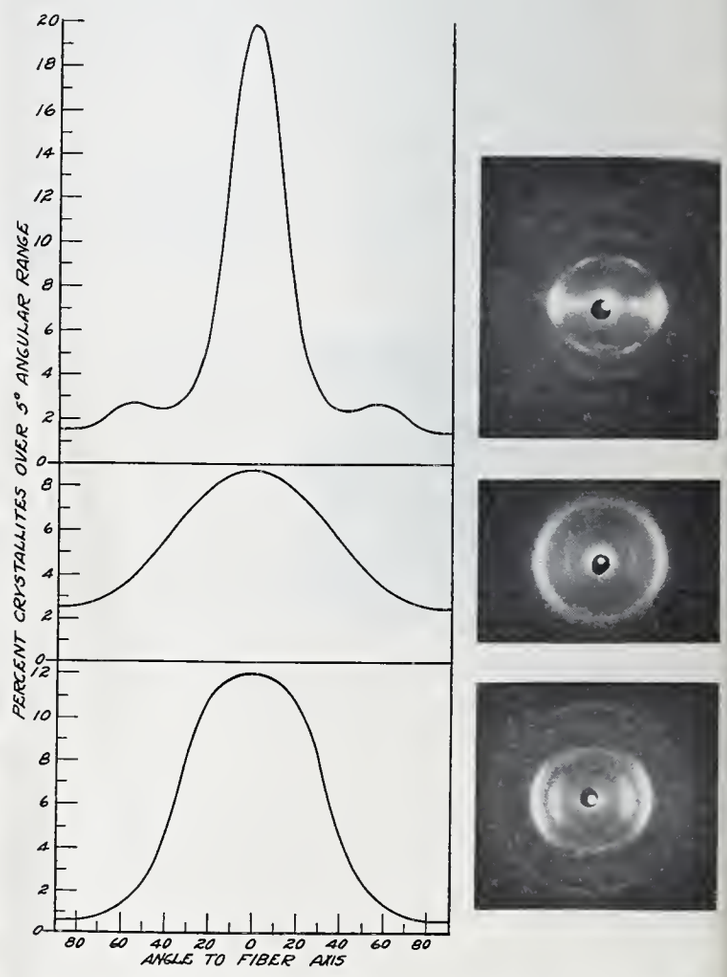

Figure 6. Typical Orientation Curves for Cotton Mercerized with and without Tension

(Upper, mercerized with tension. Center, mercerized without tension. Lower, unmercerized)

percentage basis and plotted in terms of crystallite orientation.

The curves obtained by this method give a measure of the average orientation of a number of fibers, since the diffraction pattern is usually made from a bundle of a thousand or more fibers. All fibers do not give normal distribution curves corresponding to an irregular arrangement of the crystallites such as found in rayon (*6*) and to a more or less degree in cotton (*10*). In some fibers the crystallites have a degree of regularity in their inclination to the fiber axis. This is especially true in certain types of wood known as compression wood (*30*) such as shown in Figure 5. This is contrasted with ramie which has a majority of crystallites oriented parallel to the fiber axis.

Figures 6 and 7 show the type of curves obtained for several other different materials.

As a rule the curves do not fit any simple mathematical equation, but correspond to normal frequency curves which are most satisfactorily differentiated from one another by statistical methods (*16*, *29*, *37*). The exact method of treatment depends upon the type of curve and the nature of the information desired. Preliminary results indicate that many properties are proportional to the sine or cosine of the mean, median, or standard deviation of the crystallites. The curves may also be expressed in terms of per cent orientation (*25*).

Another method is that of obtaining a factor which represents a summation of the behavior of groups of crystallites over the whole angular range. If the relative number of crystallites over each 5° angular range is multiplied by the sine or cosine of the average angle, the product is proportional to the behavior of this group and the summation of all the groups gives a factor which represents the general behavior of the fibers. For cosine values this gives a factor which varies from 100, when the crystallites are all parallel to the fiber axis, to 50 when they have random arrangement. This method works satisfactorily for the correlation of properties which are anisotropic and consequently proportional to the sine or cosine of their angle to the fiber axis.

Figure 8 shows the orientation curves for three commercial grades of cotton which differ in physical and microscopic properties. The application of the various methods mentioned above for differentiating between the orientation of these samples is illustrated in Table II.

Table II. Methods for Expressing Differences in Orientation of Cottons

Method	Values		
	Irrigated cotton	Eastern cotton	Egyptian cotton
Tensile strength of cord	17.6	18.3	20.0
Height of mode	11.40	12.00	13.35
Per cent orientation	45.06	49.94	52.86
Cosine summation factor	85.38	87.79	88.58
Median	17.83°	16.41°	14.38°
Mean	27.27°	25.50°	24.10°
Standard deviation	32.40°	29.30°	28.40°

Discussion

The work now in progress employing this method is of a twofold nature: First, the orientation of the crystallites is being correlated with the orientation of the gross configurations of the fiber as revealed under the microscope with ordinary and polarized light (*8*), and by such a study it is hoped to obtain fundamental information regarding the arrangement of the cellulose units in the cell walls of fibers. The results obtained by this method are also being compared with those obtained by optical methods (*25*).

The second application is concerned with a study of the relation between orientation and the various physical and chemical properties of the cellulose fiber. The experimental data thus far obtained indicate a functional relationship between the orientation of the crystallites and many physical properties, and it is possible that with the compilation of further data a definite mathematical relationship may be found in many cases. It is obvious, however, that other factors such as the nature of the wall configurations in certain fibers (*1*), the arrangement of the crystallites in these larger structural

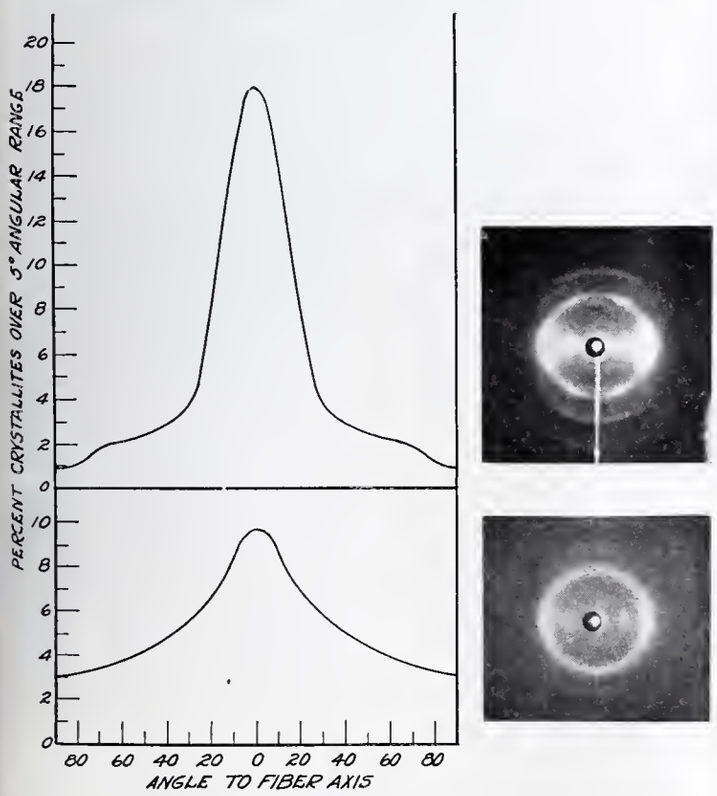

Figure 7. Typical Orientation Curves for Two Types of Rayon

(Upper, cuprammonium rayon. Lower, viscose rayon)

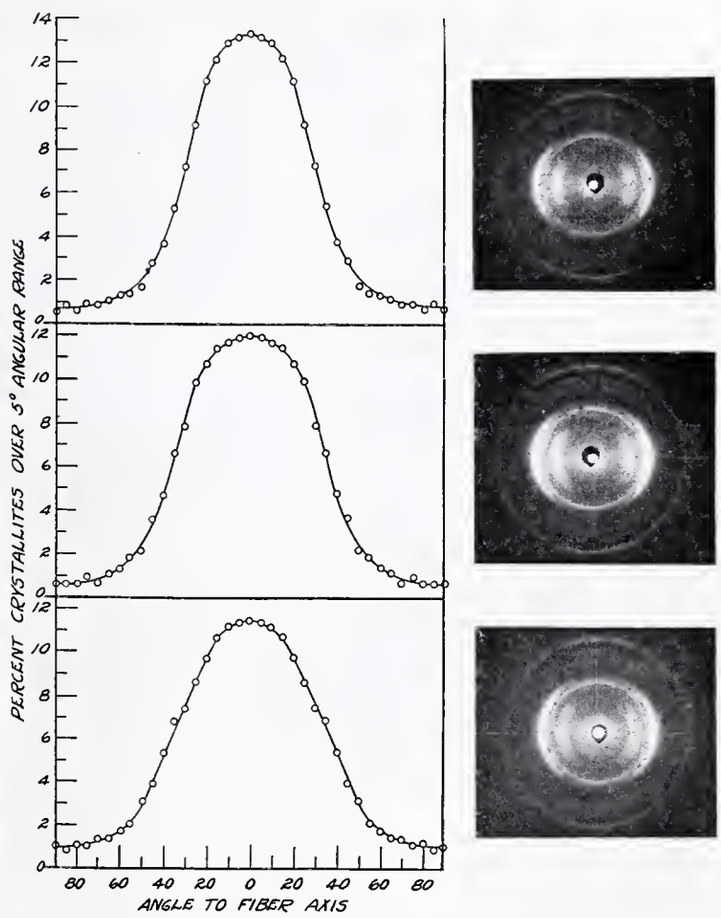

Figure 8. Orientation of Crystallites in Three Types of Cotton

(Upper, Egyptian cotton. Center, eastern cotton. Lower, irrigated cotton)

units (*34*, *35*), the shape and size of the crystallites as well as the attraction forces between them, and the nature and the amount of the intercrystalline material will also have considerable influence upon the properties of the fiber. This will necessitate a consideration of the chemical constitution and microscopic structure of the fiber in connection with x-ray studies in order properly to interpret the x-ray results. Such studies are in progress and the modifications and limitations of the above general method when applied to specific fibers will be described in future publications concerning the application of this method to different types of fibers and to specific problems relating to these fibers. It is obvious that the method described in this paper is not limited to cellulose fibers but may be applied equally well to protein fibers, regenerated cellulose sheets, cold-worked metals, or any other material having a fiber structure.

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Colorimetric Determination of Fluorine

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Fluorine in solution is determined by its fading action on the color of ferric acetylacetone. The influence of the acidity of the solution and of the presence of certain impurities is eliminated by determination of the fading caused by the fluorine in an aliquot of the solution, followed by a measurement of the fading produced by an equal aliquot to which has been added a known quantity of fluorine. The fluorine content of the aliquots is calculated from the ratio of the fading of the unknown to that of the known, multiplied by the quantity of fluorine added in the second case.

The determination of fluorine in silicon tetrafluoride distillates from a highly simplified apparatus (*1*) required the development of a method with which sulfates and salts of volatile acids would not interfere. Soluble fluorides in neutral or slightly acid solution react with ferric iron to form a complex which does not develop a color with the various reagents for iron. The colorimetric titration method based on this fact, as developed by Guyot (*6*) and Greef (*5*), has undergone considerable modification, chiefly by Treadwell and Köhl (*8*), and by Fairchild (*3*). The procedure to be reported is an application of the same principle, but it allows the determination of microquantities of fluorine in the presence of substances which interfere with other methods.

Attempts were made to adapt the principle directly to colorimetric procedure. Solutions of ferric thiocyanate, partially faded by various amounts of fluorine, were compared with similar solutions containing standard amounts of fluorine or no fluorine at all. Similar trials were made in which salicylic acid, 8-hydroxy quinoline, and acetylacetone were substituted for thiocyanate as color reagents for iron. Since these experiments were published (*2*), Foster (*4*) has reported a procedure developed on somewhat similar principles, using thiocyanate as a color reagent for iron. However, the colored compounds formed by iron and its color reagents previously listed, with the exception of acetylacetone, fade appreciably in a short time. Furthermore, the degree of fading caused by a unit amount of fluorine on all of the colored iron compounds is markedly altered by slight changes in the acidity of the solution. It is very difficult to adjust the acidities of different solutions with sufficient exactness to permit reproducible results to be obtained with small amounts of fluorine. A buffer with a pH slightly under 7 which did not itself affect the colored iron compound was not found. While the method already outlined and as reported by Foster can be applied with fairly accurate results when the necessary factors can be controlled, in the procedure here reported there is no necessity for observing these difficult precautions. The color developed by ferric iron and acetylacetone has been made the basis of a colorimetric method for iron determination by Pulsifer (*7*). The stability of the compound

formed and its specificity in the presence of impurities makes acetylacetone a superior reagent for iron.

Principle of Method

It was found empirically when the conditions described under Procedure were used that plotting the colorimeter readings of solutions of ferric acetylacetone faded by quantities of fluorine up to 0.4 mg. against the fluorine content of each solution gives a straight line (curve 1 in Figure 1). The slope of this line is altered by changes in the acidity of the solutions and by certain other substances. It is therefore necessary to prepare a standard having the same acidity and concentration of impurities as the unknown by adding to an aliquot of the unknown solution a known quantity of fluorine. The reading of the unknown, subtracted from the reading of the unknown plus 0.1 mg. fluorine, gives the fading caused by the known quantity of fluorine.

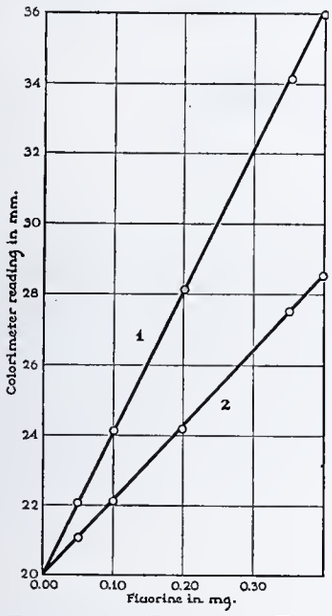

Figure 1. Fading of Ferric Acetylacetone by Different Amounts of Fluorine

Theory would demand that the data from such an experiment as that indicated in curve 1, Figure 1, should give a hyperbola when plotted if the solutions obeyed Beer's law and the colored element suffered no change on dilution. Evidently there are equilibrium conditions in solutions of ferric acetylacetone and fluorine such that the fluorine and acetylacetone compete for the iron and each added increment of fluorine meets with a more severe competition.

Apparatus and Procedure

Colorimeter. A light filter such as the blue Bausch and Lomb 3610 must be used in the eyepiece of the Duboscq colorimeter, since the colors of solutions containing different concentrations of ferric acetylacetone vary from red to yellow and cannot be matched directly.

Ferric Chloride. Prepare a solution of ferric chloride containing 0.3 mg. iron per cc. Protect it from light during use and discard after 2 to 3 hours.

Acetylacetone. Prepare a 0.5 per cent aqueous solution from the freshly distilled product.

Standard Fluorine Solution. Prepare a solution containing 0.1 mg. fluorine per cc. from sodium fluoride of known purity.

If the solution contains carbonates, add a few drops of phenolphthalein and introduce 0.1 *N* hydrochloric or nitric acid dropwise to the boiling solution until it no longer turns pink on further boiling. Immediately make the solution slightly alkaline with 0.1 *N* sodium hydroxide and allow it to cool in a stoppered flask. Make this, or a solution not containing carbonates, just acid to phenolphthalein and add a drop of dilute acid (1 to 100). To each of two 25-cc. volumetric flasks transfer 1 cc. of the ferric chloride and 1 cc. of the acetylacetone solutions. (It seems probable that a stock solution of ferric acetylacetone could be employed, but the writer has not tested such a procedure.) Add an aliquot of the unknown solution containing not over 0.25 mg. fluorine to one flask, and dilute both flasks to volume. Compare the solutions in the colorimeter with the solution containing no fluorine set at 20 mm. in the left cup. Take twenty readings by increasing the depth of the solution in the right cup and average the results. Repeat the procedure with the same size aliquot of the unknown solution, adding 1 cc. (0.1 mg. fluorine) of the standard solution of sodium fluoride to the flask containing the unknown. Again take twenty readings, as before, and determine the average. Calculate the results according to the equation:

$$F = \frac{(X - 20)\ D\ 0.1}{(Y - X)}$$

where F represents the fluorine content of the total solution in milligrams, X is the reading of the unknown, Y is the reading of the unknown plus 0.1 mg. fluorine, and D represents the ratio of the total volume of the solution to the volume of the aliquots.

The results of some analyses of sodium fluoride solutions are given in Table I. The fading caused by a unit amount of fluorine varies slightly because of the pH of the solutions and, in some cases, due to the fact that different solutions of ferric chloride were used in the separate analyses.

Table I. Analysis of Sodium Fluoride Solutions

Reading of Unknown	Reading of Unknown + 0.1 mg. F	F Found in Total Solution	F Present[a] in Total Solution
Mm.	*Mm.*	*Mg.*	*Mg.*
24.45	28.88	0.500	0.500
24.45	28.90	0.500	...
24.30	28.71	0.485	...
24.44	28.90	0.495	...
22.16	26.55	0.245	0.250
22.14	26.45	0.245	...
20.84	25.01	0.100	0.100
20.74	24.44	0.100	...
20.40	24.41	0.045	0.050

[a] The aliquots in all cases represented one-fifth of the total volume of the solution.

Limitations of Method

The effect of salts of volatile acids and other substances likely to be present in silicon tetrafluoride distillates and other fluoride solutions has been investigated. One-tenth gram sodium chloride and 0.2 gram sodium sulfate alter the color of ferric acetylacetone, but 0.05 gram of the first salt and 0.1 gram of the second, either alone or together, are without influence on the colored compound. Therefore, the aliquots of the unknown solution should not contain more than the latter amounts of these two salts. Sodium nitrate up to 0.4 gram and saturated silicic acid up to saturation are without effect on the color of ferric acetylacetone. The solution must be neutral or slightly acid and must contain no ion which forms a precipitate or undissociated salt with ferric iron or with fluorine.

Table II. Analyses of Sodium Fluoride Solutions Containing Impurities

Reading of Unknown	Reading of Unknown + 0.1 mg. F	F Found in Total Solution	F Present[a] in Total Solution
Mm.	*Mm.*	*Mg.*	*Mg.*
21.11	22.24	0.490	0.500
21.26	22.53	0.495	...
20.61	21.84	0.245	0.250
20.58	21.74	0.250	...
20.58	21.75	0.250	0.250

[a] The aliquots in all cases represented one-fifth of the total volume of the solution Each contained 0.1 gram Na_2SO_4, 0.1 gram $NaNO_3$, 0.04 gram NaCl, and 5 cc. saturated silicic acid.

Of the substances mentioned above only sodium sulfate reduces or alters in any other way the fading action of fluorine on the color of ferric acetylacetone. Curve 2, Figure 1, shows the results of two experiments similar to the one whose results are recorded as curve 1, except that the aliquots of

the fluoride solutions in one case contained 0.1 gram sodium sulfate, and in the other, 0.1 gram of the same salt and also 0.1 gram sodium nitrate, 0.04 gram sodium chloride, and 5 cc. saturated silicic acid. The colorimeter readings in the two experiments agreed within experimental limits and are therefore plotted as one curve. Curve 1 shows the results when the aliquots contained no impurities and when they contained 0.1 gram sodium nitrate, 0.04 gram sodium chloride, and 5 cc. saturated silicic acid. Although the effect of sodium sulfate is to reduce the degree of fading of ferric acetylacetone caused by fluorine, and to render the procedure less sensitive, the accuracy of the results is not materially affected, as is evident from Table II. Later experiments have shown that the sulfate collected in the receiver of a simplified silicon tetrafluoride evolution apparatus (*1*) is not sufficient to alter appreciably the fading action of fluorine on the colored substance.

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Determination of Pyridine Bases in the Presence of Ammonia

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The crude gas from by-product coke ovens contains considerable quantities of the vapors of pyridine, quinoline, isoquinoline, and their homologs. The "tar bases" of higher boiling points are, for the most part, condensed with the tar, but considerable quantities of the vapors of the more volatile bases are carried forward into the ammonia saturator and are there absorbed as their sulfates. The concentration of the sulfates of the organic bases in the saturator bath liquor finally attains a concentration at which the rate of removal of the tar bases as impurities on the crude ammonium sulfate becomes equal to the rate of introduction into the bath.

The accurate determination of the tar bases in saturator bath liquor and in crude ammonium sulfate is rendered difficult by the presence of ammonium sulfate in large excess and by the wide variation in the basicities of the individual bases. Some of these compounds are so very weakly basic

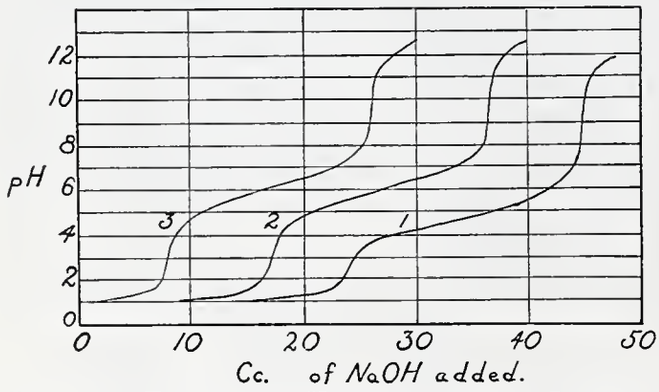

Figure 1. Titration of Hydrochlorides of Pyridine Bases

1. Pyridine hydrochloride
2. α-Picoline hydrochloride
3. β-Picoline hydrochloride

that their salts are largely hydrolyzed in neutral solution; others are almost as strongly basic as is ammonia and can be liberated only by making the solution so strongly alkaline that most of the ammonia is set free. One method that has been used to determine pyridine bases in saturator bath liquor is to treat a measured volume of the solution with an excess of sodium hydroxide, distill the ammonia and tar bases into a dilute acid solution, render this solution alkaline, and add an excess of a solution of sodium hypobromite to oxidize the ammonia, distill the tar bases into standard acid, and titrate the excess of acid with standard alkali, using methyl orange or some other indicator sensitive to weak bases. This method is not very satisfactory. A large amount of the hypobromite solution must be added to oxidize the large excess of ammonia, the recovery of the bases is often incomplete, and the end point in the final titration is not a sharp one. Various expedients for minimizing these disadvantages have been suggested (*1*, *2*) but no really satisfactory method has been described for determining tar bases in the presence of large amounts of ammonium salts.

The authors have found that the various tar bases can be determined by electrometric titration and that this procedure eliminates some of the disadvantages inherent in the older methods.

Preliminary Experiments

One hundred cubic centimeters of an approximately 0.25 *N* solution of pyridine in dilute hydrochloric acid were titrated with approximately normal standard solution of sodium hydroxide. After each addition of the standard alkali the pH of the solution was measured, using a quinhydrone electrode and balancing against a saturated calomel electrode. Preliminary experiments had shown that the standard hydrogen electrode is rapidly poisoned by pyridine and other organic bases and by some of the impurities that are normally present in saturator bath liquor. For this reason the quinhydrone electrode was used, despite its liability to error in strongly alkaline solutions. Within the range of pH encountered in the authors' work the quinhydrone electrode gave results that were entirely satisfactory for the accurate determination of the tar bases, although in a few cases the absolute values of the pH at the extreme alkaline end may be in error.

The results obtained in the potentiometric titration of pyridine by sodium hydroxide are shown by curve 1 on Figure 1. Free pyridine begins to be liberated when the pH of the solution reaches 2.8; the liberation of pyridine is complete at a pH of about 8.5. The break that indicates the beginning of the liberation is not extremely sharp. Pyridine is such a weak base that its hydrochloride is hydrolyzed to a very considerable extent. The difficulty of determining pyridine ac-

curately by titration with an indicator is evident. Few indicators show color change at the point corresponding to the liberation of pyridine and at this point the rate of change of pH with addition of alkali is so small that no sharp end point can be obtained.

By potentiometric titration, satisfactory results can be secured. In one series of experiments, the results were as follows:

Pyridine Taken	Pyridine Found
Grams	*Grams*
1.920	1.918
1.920	1.917
1.920	1.920
2.179	2.183

Similar titrations were made with solutions of pure α-picoline, β-picoline, lutidine, symmetrical collidine, and quinoline. The lutidine used was a mixture of various dimethyl pyridines. The results were as follows:

Compound	Taken	Found
	Grams	*Grams*
α-Picoline	2.105	2.104
β-Picoline	2.093	2.090
Lutidine	2.106	2.107
Collidine	1.888	1.885
Quinoline	4.247	4.250

The titration curves for these compounds are shown by Figures 1, 2, and 3.

The basicity of the homologs of pyridine increases with the number of the substituted methyl groups. Collidine is almost as strongly basic as ammonia. In order to liberate the higher homologs completely in a solution containing large amounts of ammonium salts, the solution must be made so strongly alkaline that a very considerable amount of ammonia is also set free. Several methods of analysis have been suggested in which the tar bases are liberated and separated from the ammonia by making the solution very faintly alkaline and then distilling. It is evident that no such method will separate the higher homologs of pyridine sharply from the ammonia. Quinoline is a weaker base than pyridine, and shows a less abrupt rise in pH at the point at which the liberation of the free base begins.

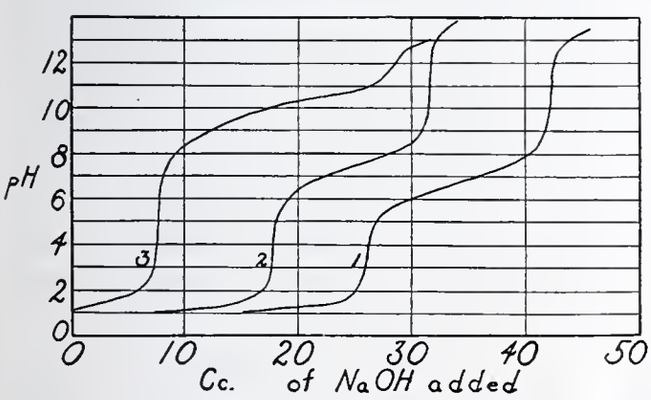

Figure 2. Titration of Higher Bases and of Ammonia

1. Lutidine hydrochloride
2. Collidine hydrochloride
3. Ammonium chloride

In the titration of a solution containing a mixture of the various bases, the initial break in the curve comes at pH corresponding to the beginning of the liberation of the weakest base that is present. Since the liberation of the weaker bases is not complete at a pH below that at which some of the higher homologs begin to be set free, the titration curve for the mixture does not show a series of distinct steps corresponding to the successive liberation of the various individual compounds. There is a continuous rise in pH from the neutralization point for the weakest base to the point at which the most strongly alkaline of the compounds is liberated. Mixtures of the hydrochlorides of the various bases with ammonium chloride were titrated potentiometrically with a standard solution of sodium hydroxide. The total volume of the solution in each case was 125 cc. The solutions used contained the following amounts of materials:

Solution

1 Pyridine, 1.920 grams; ammonium chloride, 1.257 grams
2 Lutidine, 2.107 grams; ammonium chloride, 1.257 grams
3 Collidine, 1.888 grams; ammonium chloride, 1.257 grams
4 Quinoline, 4.247 grams; ammonium chloride, 1.257 grams
5 Pyridine, 0.3866 gram; α-picoline, 0.4216 gram; β-picoline, 0.4019 gram; lutidine, 0.4211 gram; collidine, 0.3776 gram; quinoline, 0.8494 gram; NH_4Cl, 0.5026 gram

The results of these titrations are shown on Figures 4 and 5. It is apparent that solutions that contain pyridine or quinoline but none of the higher homologs can be titrated potentiometrically even in the presence of ammonium salts, although the point at which the liberation of the organic base is complete and the liberation of ammonia begins is not extremely sharp. In the presence of even small amounts of the higher homologs the break between the organic base and the ammonia practically disappears. In the analysis of a solution containing lutidine or collidine the ammonia must be removed before the tar bases can be titrated electrometrically.

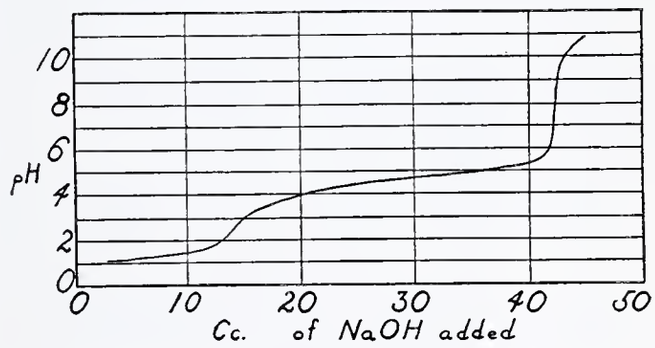

Figure 3. Titration of Quinoline Hydrochloride

Proposed Method of Analysis

Based on these preliminary experiments, the following method was developed for the determination of the pyridine bases in the presence of ammonia.

Transfer a portion of the solution to be analyzed, sufficient to contain about 2.5 grams of pyridine bases, to a separatory funnel, add 25 cc. of xylene, and add a considerable excess of a concentrated solution of sodium hydroxide. Shake well, let settle, and separate the layer of xylene. Extract the aqueous layer with four more successive 25-cc. portions of xylene. Extract the combined xylene solutions with six successive portions of 25 cc. each of 10 per cent hydrochloric acid. Transfer the combined acid extract to a 1000-cc. Kjeldahl flask, make alkaline with a concentrated solution of sodium hydroxide, and add 100 cc. of a solution of sodium hypobromite prepared by adding 25 cc. of bromine to a solution of 100 grams of sodium hydroxide in one liter of water. Distill and collect the distillate in a beaker containing about 250 cc. of approximately 2 *N* hydrochloric acid. When 150 cc. of distillate have been obtained, discontinue the distillation, transfer the distillate to a 500-cc. measuring flask, and make up to the mark with distilled water. Titrate 100-cc. portions of this solution with approximately normal standard alkali, using a quinhydrone electrode balanced against a saturated calomel electrode. Plot the values of the pH as ordinates against the corresponding amounts of the standard solution of sodium hydroxide that have been added. The volume of the standard solution equivalent to the pyridine bases present is equal to the amount added between the break corresponding to the complete neutralization of the free acid present and the break corresponding to the complete liberation of the organic bases. In the analysis of any particular set of samples containing a mixture of bases, the weight of the mixed bases corresponding to 1 cc. of the solution of sodium hydroxide should be determined in a separate experiment. The bases from a comparatively large amount of the material should be liberated, collected, purified,

and dried, and a standard solution containing a known concentration of the pure dry bases should then be titrated with the sodium hydroxide solution in the usual manner.

In the method described, the extraction with xylene serves to collect all of the organic bases and at the same time eliminates most of the ammonia set free upon the addition of alkali to the original solution. The small amount of ammonia that is carried through into the solution obtained by the extraction of the xylene solution with hydrochloric acid is readily and completely oxidized by the sodium hypobromite. To prove that the elimination of the ammonia is complete, a portion of a strong solution of ammonium sulfate, free from pyridine bases, was subjected to the method of analysis outlined above. In the final electrometric titration the amount of alkali required was exactly equivalent to the free acid in the

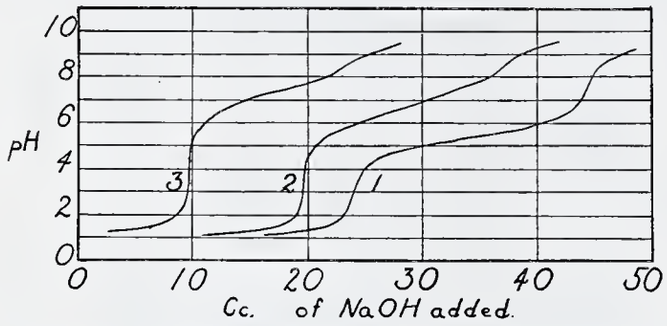

Figure 4. Titration of Hydrochlorides of Organic Bases in Presence of Ammonium Chloride

1. Pyridine
2. Lutidine
3. Collidine

known volume of standard hydrochloric acid in which the final distillate was collected. None of the ammonia was therefore carried through into the final solution that was titrated.

To prove that all the pyridine contained in the original sample is carried through into the final solution that is titrated, a known volume of a solution of pyridine hydrochloride containing a known concentration of pyridine was subjected to the regular method of analysis. The following results were obtained:

Pyridine Taken	Pyridine Found
Grams	*Grams*
1.920	1.909
1.920	1.914

Analysis of Saturator Bath Liquor

A sample of the bath liquor from the ammonia saturator of the By-Product Coke Oven Plant of the Rochester Gas and Electric Company was analyzed by the method described above. A sample of 200 cc. of the original solution was taken for analysis. On the addition of sodium hydroxide, some solid sodium sulfate separated. This was redissolved by the addition of water. In the extraction of the alkaline solution with xylene, a layer of sludge was formed between the xylene and the aqueous layer. This was always drawn off along with the aqueous layer. Any sludge formed in the extraction of the xylene with hydrochloric acid was allowed to remain behind with the xylene layer. In each of two duplicate determinations 17 cc. of the standard alkali were required in the final titration.

In order to determine the equivalent of the standard solution of sodium hydroxide in terms of the bases actually present in the saturator bath, a solution containing a known concentration of the purified bases from the bath liquor was titrated with the standard solution of alkali.

About 3 liters of the bath liquor were made strongly alkaline with sirupy sodium hydroxide and the layer of liberated bases was separated. The aqueous layer was extracted five times with separate portions (100 cc.) of a mixture of benzene and toluene. The combined extract was shaken with five successive 50-cc. portions of 15 per cent hydrochloric acid. The combined acid solution was made strongly alkaline with sodium hydroxide, and the separated bases were added to the original lot of bases that was obtained from the original bath liquor. The aqueous layer was again extracted with the mixture of benzene and toluene, and the resulting solution was shaken with five portions of 20 cc. each of dilute hydrochloric acid. The acid solution was made strongly alkaline and the small amount of separated bases was combined with the bases previously obtained. The extraction with benzene and toluene and with acid was repeated and a final and very small amount of free base was obtained.

The combined bases were distilled to dryness and the distillate was dried with solid sodium hydroxide. The dry material was then again distilled through a fractionating column.

The results obtained in this distillation were as follows:

Temperature	Distilled
° C.	%
90	Start
115	15
120	55
135	74
150	79
165	81
185	87
189 (dry)	92

From the distillation it appears that the mixed bases contained about 50 per cent of true pyridine and about 25 per cent of picoline, the remainder being composed of a mixture of the higher bases.

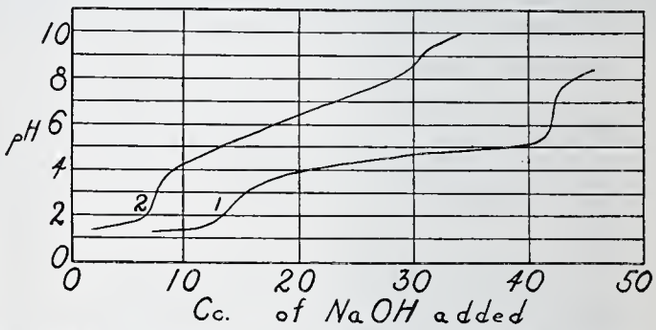

Figure 5. Titration of Hydrochlorides of Organic Bases in Presence of Ammonium Chloride

1. Quinoline
2. Mixture of various bases

Of the redistilled bases, a sample weighing 20.079 grams was transferred to a Kjeldahl flask, 180 cc. of water and 100 cc. of a solution of sodium hypobromite were added, and the ammonia-free bases were distilled and collected in dilute acid. The solution was diluted to 500 cc. and portions of 100 cc. each were withdrawn for titration with 1.1925 *N* sodium hydroxide solution. The bases present in the sample were equivalent to 35.1 cc. of the alkaline solution. Thus 1 cc. of a normal solution of sodium hydroxide was equivalent to 0.09595 gram of the mixed bases. Since 200 cc. of the original saturator bath liquor required 17 cc. of the standard alkali, the bath liquor contained 0.9726 gram of bases in 100 cc., or 0.08116 pound of bases per gallon.

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Determination of Titanium in Plain-Carbon, High-Chromium, and 18 Chromium–8 Nickel Steels

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THE addition of titanium to high-chromium steel and also to 18 chromium–8 nickel steel has necessitated the development of a rapid, accurate method for determining this element. The method here described can be worked in 1 to 1.25 hours and comprises the solution of the sample in dilute sulfuric acid, precipitation of the titanium with cupferron in the presence of the ferrous iron, filtration, ignition, and completion of the determination colorimetrically. The colorimetric method for titanium is based on the light-straw to amber color developed when hydrogen peroxide is added to a sulfuric acid solution containing titanium; it is limited to solutions containing not more than 0.1 mg. of titanium per cc.

Procedure

One-half to 1 gram of the sample of drillings is treated in a 150-cc. covered beaker with 100 cc. of 10 per cent sulfuric acid and the liquid heated gently until all action appears to have ceased. The solution is cooled to approximately 20° C., some ashless paper pulp is introduced, and a cold, freshly prepared, 6 per cent solution of cupferron (ammonium nitrosophenylhydroxylamine, $C_6H_5N \cdot NO \cdot ONH_4$) is added dropwise, with constant stirring, until the precipitate just assumes a reddish brown color. Additional cupferron only causes more iron to be precipitated. The precipitate, which contains all of the titanium, together with a small amount of iron, is filtered on an 11-cm. paper containing a considerable amount of ashless paper pulp, washed 12 to 15 times with cold 5 per cent sulfuric acid, and then 5 times or more, if the steel is known to contain small percentages of molybdenum or tungsten, with 5 per cent ammonium hydroxide. The paper and residue are transferred to a 50-cc. platinum crucible and ignited at a temperature just sufficient to destroy the carbon of the filter paper. The contents of the crucible are fused with approximately 1 gram (a sufficient amount) of potassium pyrosulfate and the melt is dissolved in 25 cc. of 10 per cent sulfuric acid. The solution is transferred to a Camp comparison tube, cooled to room temperature, and the titanium determined colorimetrically in the following manner:

Colorimetric Determination

Three cc. of 3 per cent hydrogen peroxide are added and the solution is mixed, which will result in the development of a light-straw to amber color, proportional in intensity to the amount of titanium present. To the other comparison tube there is added 25 cc. of cold 10 per cent sulfuric acid, the same amount of potassium pyrosulfate as used to make the fusion, 3 cc. of hydrogen peroxide, and from a 10-cc. buret a measured amount of standard titanium sulfate solution (1 cc. = 0.0005 gram titanium) which contains slightly less titanium than the sample. The volume of the standard is then made equal to that of the sample by the addition of the necessary amount of 10 per cent sulfuric acid. The color of the standard should now be slightly less intense than that of the sample. Equal additional volumes of the standard titanium solution and of 10 per cent sulfuric acid are then added to the standard and sample, respectively, each of the solutions being mixed and compared after each addition until the colors of the two solutions match exactly. The number of cubic centimeters of the standard titanium sulfate used, multiplied by 0.0005 and by 100, and divided by the weight of sample taken, gives the percentage of titanium in the steel.

In case the steel contains an appreciable amount of copper, the hot sulfuric acid solution of the sample is filtered on a 9-cm. paper containing a small amount of ashless paper pulp, and the filter paper and residue washed well with 10 per cent sulfuric acid. The filtrate is cooled to about 20° C. and the cupferron precipitation made as described in the second paragraph.

The paper holding the sulfuric-acid insoluble and metallic copper is transferred to a 250-cc. beaker, treated with 25 cc. of nitric acid (sp. gr. 1.135), and the solution warmed to dissolve the copper. Approximately 50 cc. of hot water and a slight excess of ammonium hydroxide are introduced, the solution heated to boiling, filtered, and the paper and precipitate washed well with hot water. The precipitate is ignited at a low temperature to burn off the carbon of the filter paper, added to the ignited cupferron precipitate, and the combined precipitates fused with potassium pyrosulfate. The melt is dissolved in 10 per cent sulfuric acid, and the titanium determined colorimetrically as previously described.

Should the steel be known to contain vanadium, the ignited cupferron precipitate is transferred to a 100-cc. platinum dish, treated with 5 cc. of hydrofluoric acid (48 per cent) and 10 cc. of perchloric acid (60 per cent) and the solution evaporated on a sand bath until the volume has been reduced to 5 cc. or less. Any chromium carbide that fails to dissolve during the solution of the sample in sulfuric acid will be rendered soluble by the strong fuming with perchloric acid. The solution is diluted with warm water to 50 cc., treated with an excess of 5 cc. of 10 per cent sodium hydroxide, boiled for several minutes, and filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot water, ignited, fused with a small amount of potassium pyrosulfate, and the determination completed for titanium as described. The vanadium and chromium pass into the filtrate as soluble sodium vanadate and sodium chromate.

In the event the titanium content of the steel is sufficiently high to render the color method impractical, the determination is carried out as follows:

Alternate Method

One gram of the sample is dissolved and the cupferron precipitation made as described in the second paragraph. The paper and precipitate are transferred to a platinum dish and ignited at a temperature just sufficient to destroy the carbon of the paper. The contents of the dish are treated with 5 cc. of hydrofluoric acid (48 per cent) and 10 cc. of perchloric acid (60 per cent) and the liquid evaporated on a sand bath to the complete expulsion of all perchloric acid. The perchloric acid residue is fused with several grams (as sufficient amount) of sodium pyrosulfate and the melt dis-

solved in 50 cc. of 10 per cent sulfuric acid. An excess of 5 cc. of 10 per cent sodium hydroxide is added, the solution boiled for several minutes, and filtered on a 9-cm. paper. The paper and precipitate are washed thoroughly with hot water. Any vanadium present is converted to sodium vanadate and will pass into the filtrate. The precipitate is dissolved off the paper with 25 cc. of hot sulfuric acid (1 to 4) and the filter washed well with hot water.

Titanium Recovered from Titanium-Free Steels Salted with Known Amounts of Titanium Sulfate

Expt.	Kind of Steel	Steel Taken	Titanium Added	Titanium Found	Error
		Grams	*Gram*	*Gram*	*Gram*
1	18-8	0.5	0.0033[a]	0.00335	+0.00005
2	Ingot iron	0.5	0.0030	0.00297	−0.00003
3	6% Cr	0.5	.....	0.0045 0.0045	.....
4[b]	6% Cr	0.5	.....	0.0036	.....
5[b]	6% Cr	0.5	.....	0.0035	.....
6	6% Cr-8% V	0.5	0.00265	0.00260	−0.00005
7	Std. No. 82 Ni-Cr cast iron[c]	2	.....	0.0010	.....

[a] A result of 0.0033 gram titanium was obtained by the second procedure described.
[b] A result of 0.72 per cent titanium was obtained on 1 gram of this sample by the second procedure described.
[c] The Bureau of Standards obtained 0.048 per cent titanium on this sample against our result of 0.05 per cent by color.

The solution obtained as described in the preceding paragraph (which will contain all of the titanium) is treated with 1 gram of tartaric acid, made ammoniacal and then acid with an excess of 2 cc. of sulfuric acid (sp. gr. 1.84) per 100 cc. of solution. The liquid is saturated with hydrogen sulfide and if any precipitate forms it is filtered on a 9-cm. paper containing some ashless paper pulp, washed thoroughly with hydrogen sulfide water containing 1 per cent sulfuric acid and 1 per cent tartaric acid, and discarded. An excess of 2 cc. of ammonium hydroxide (sp. gr. 0.90) is then added to the filtrate and hydrogen sulfide is passed through the liquid for 5 minutes longer. Some ashless paper pulp is added, the solution filtered on a 9-cm. paper, and the precipitate of ferrous sulfide washed well with ammonium sulfide water containing 1 per cent ammonium sulfate and 1 per cent ammonium tartrate, and discarded. The filtrate (having a volume of approximately 150 cc.) is boiled to expel hydrogen sulfide, acidified with an excess of 30 cc. of sulfuric acid (1 to 1), and cooled to 20° C. Some ashless paper pulp is introduced and the titanium is precipitated by the addition, dropwise and with constant stirring, of a cold, freshly prepared, 6 per cent solution of cupferron. An excess of the reagent is indicated by the formation of a snow-white precipitate which rapidly disappears. The titanium precipitate is filtered on an 11-cm. paper containing some ashless paper pulp, washed twelve to fifteen times with cold 5 per cent sulfuric acid, and then five times with 5 per cent ammonium hydroxide. The paper and precipitate are transferred to a platinum crucible and ignited, first at a low temperature and finally at 1050° to 1100° C., cooled, and weighed. The weight of titanium oxide found, multiplied by 59.95, and divided by the weight of sample taken, gives the percentage of titanium in the steel. If desired, the titanium oxide may be fused with a small amount of potassium pyrosulfate, the melt dissolved in 100 cc. of 6 per cent sulfuric acid, and the warm solution (about 75° C.) passed through a zinc reductor into ferric sulfate solution [prepared by dissolving 100 grams of ferric sulfate in 150 cc. phosphoric acid (sp. gr. 1.72), and 850 cc. of water containing 20 cc. of (1 to 1) sulfuric acid], the resulting ferrous sulfate then being titrated with standard 0.05 N potassium permanganate (1 cc. = 0.002395 gram titanium). Approximately 100 cc. of 2.5 per cent sulfuric acid are first passed through the reductor [12 in. (30.5 cm.) in length by 0.75 in. (19.1 mm.) in diameter] and discarded. The hot 6 per cent sulfuric acid solution containing the titanium is then passed through the reductor into 25 cc. of ferric sulfate solution and the reductor washed with three 30-cc. portions of hot 6 per cent sulfuric acid, followed by one 30-cc. portion of water to remove the last traces of titanium. When the titanium solution is passed through the reductor, the tip end of the reductor tube should dip beneath the surface of the ferric sulfate solution. A blank is run on the reductor in exactly the same way the determination was made, except that the same volume of 6 per cent sulfuric acid is substituted for the titanium solution.

To prove the accuracy of the method several samples of titanium-free steels were salted with a known amount of titanium sulfate and put through the method as described. The results obtained are given in the table.

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A Modified Soxhlet

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The depicted form of Soxhlet can be assembled from stock laboratory apparatus excepting that the rubber band C sealing the two Büchner funnels is made from an inner tube of an automobile tire. Since all sizes of used inner tubes are cheaply available, all sizes of Büchner funnels can be used; hence all practical sizes of these modified Soxhlets can be assembled. The two T tubes D, held by rubber tubing A, are connected by the rubber tubing B. The lower Büchner, supplied with closely fitting filter paper weighed down by a lead or iron ring, is charged with the material to be extracted, and the parts are adjusted with screw clamp E' closed and screw clamp E open. Heating the flask containing the solvent carries the vapor through B to the condenser which delivers the solvent into the Büchners, and gravity completes

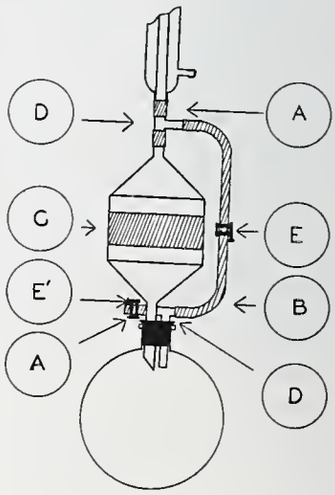

Figure 1

the circuit of the solvent. When necessary or desirable, heating can be discontinued and with screw clamp E closed, and screw clamp E' open the liquid on the solid in the Büchners can be drawn down by making connection with the vacuum pump. Ordinarily this filtering is not necessary, or may be made at the end of process of extraction.

This form of apparatus is useful for all extraction made in Soxhlets, and more especially for recrystallization of large masses by the use of limited volumes of solvents.

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Standardization of Kauri Butanol Test for Paint and Lacquer Thinners

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IN DETERMINING the suitability of a solvent as a paint and lacquer thinner, the kauri butanol test is one of the most important items in the specifications to be met. In spite of its widespread use by the paint and lacquer as well as the petroleum industry, however, the results have not been consistent, and different laboratories have at times been unable to check closer than 2 or 3 points on a solvent having a kauri butanol value of 35 to 45. The object of this investigation was to study the different variables of the kauri butanol test and to determine to what extent deviations in procedure would affect its results.

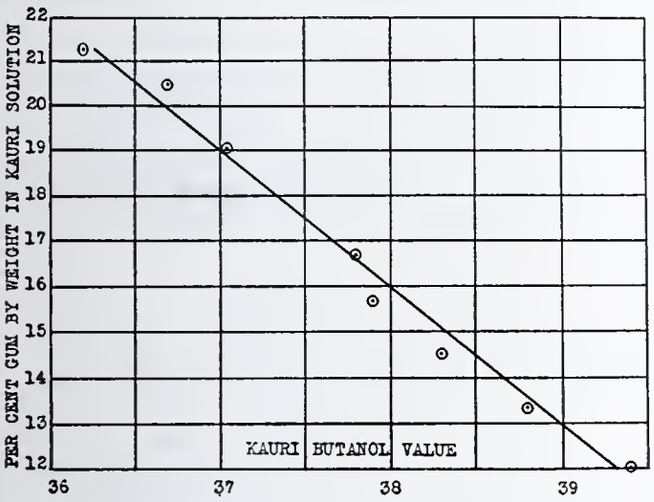

Figure 1. Effect of Gum Content on Kauri Butanol Value

It was decided at the start to follow, as closely as possible, the method adopted as official in 1931 by the Paint and Varnish Superintendents' Club of the Philadelphia District (*7*):

One hundred grams of carefully selected pulverized kauri gum are dissolved in 500 grams of butyl alcohol distilling from 114.4° to 116.6° C. (238° to 242° F.) using a water-cooled reflux condenser to facilitate solution. This mixture is then allowed to cool, and after 96 hours it is decanted into a clean, dry bottle and well stoppered.

No particular type of kauri gum is specified, and there is no assurance that two solutions made from different sources of kauri gum will have the same gum and moisture content (since gums vary in solubility and moisture). This method of preparing the solution, therefore, provided three points to be investigated: effect of the source of the kauri gum, effect of concentration of the solution, and effect of moisture in the solution.

In making the kauri butanol test, one method calls for the use of 25 cc. of kauri solution, and another for 20 grams, while in one case the materials while titrating are to be kept at 68° F. (20° C.) and in the other at 77° F. (25° C.). These varying test methods, therefore, call for two further conditions to be studied: the effect of relative amounts of kauri butanol solution used and the effect of temperature.

Effect of Source of Gum

Hosking (*5*) investigated the composition of the four types of kauri gum produced: (*a*) kauri resin freshly prepared from the tree, (*b*) the same resin after exposure to the air during 1.5 or 4.5 years (Buschharz), (*c*) fossil kauri gum (range gum), and (*d*) kauri resin obtained from the peat-moors (Sumpfharz). He concluded that the per cent of pinene (the essential oil component) decreases regularly with increasing age of the resin, the optical rotation of the pinene decreasing in the same sense. The "range gum" showed 6 per cent of a high-boiling fraction of camphor-like odor, probably fenchyl alcohol, which probably was formed from the pinene under the influence of water and salts. In case (*d*) pinene, dipentene, and fenchyl alcohol were found. Investigation of the resins left behind after the distillation of the crude resins with water showed that the amount of α-resin (low-melting resinic acids) decreases, and the amount of β-resin (high-melting resinic acids) increases with the increasing age of the crude gum.

Six samples of selected kauri gum were obtained from four different dealers in New York. Solutions of each gum were made by adding 200 grams of butanol to 50 grams of the cleaned and pulverized gum. The solutions were refluxed on a hot plate until solution appeared complete. They were then filtered through a Büchner funnel with a small amount of Sil-O-Cel to aid clarification, using suction. This produced a clearer solution than decanting after 96 hours and saved 4 days of waiting. Solutions of the same gum made by both methods gave the same kauri butanol values.

The nonvolatile content of each solution was then determined accurately by weighing out 3 to 4 grams of the solution on the lid of a quart tin can. The lids were dried in an oven at 250° F. (121.1° C.) to constant weight, which required about 2 hours.

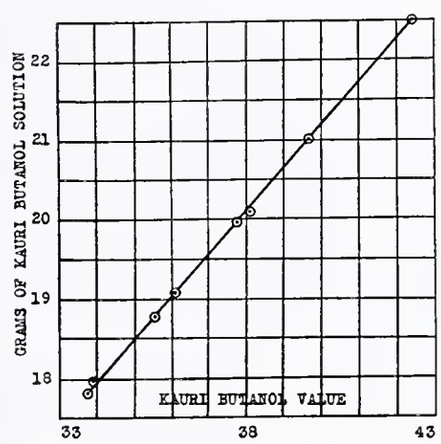

Figure 2. Effect of Relative Amount of Solution Used on Kauri Butanol Value

The gum concentration of each solution was then adjusted to 16.6 to 16.7 per cent by adding butanol, and kauri butanol values were obtained with each, using a petroleum lacquer diluent, and the official method of the Paint and Varnish Superintendents' Club of the Philadelphia District (*7*). The results appear in Table I.

Table I. Kauri Butanol Values of Gums from Different Sources

	Type of Gum	Appearance	Kauri Butanol Value
1.	Bush kauri	Light-colored chips	36.2
2.	Bush dial kauri	Large light-colored lumps, very clean	35.3
3.	Bush kauri	Light-colored chips	36.1
4.	Fossil XXX	Large dark-brown lumps	35.8
5.	No. 1 pale (probably fossil)	Large light-colored lumps, covered with dark crust	37.1
6.	Fossil	Mixture of dark and light chips	37.8

From the foregoing results it would appear that the choice of gums for the preparation of the kauri butanol solution determines to a considerable extent the kauri butanol values obtained and may produce a variation of as much as 2.5 points such as was found between solutions of samples 2 and 6.

Because of its uniform appearance, gum 2 was selected for use in all of the further work.

Effect of Concentration of Gum

A large batch of kauri butanol solution was made up, using the bush dial kauri (gum 2) in the proportion of 100 grams of gum to 500 grams of butanol. This produced a solution with a nonvolatile content of 14.6 per cent, about 2 per cent of gum being insoluble. This was increased to 16.6 per cent by boiling off the calculated amount of solvent, and incidentally producing an anhydrous solution (butanol forms a binary mixture containing 37 per cent of water and boiling at 92.3° C.). About a pint of the 16.6 per cent solution was further concentrated to 21.3 per cent. Using these two solutions and the proper amount of butanol, eight 50-gram solutions were prepared, ranging in gum content from 12.0 to 21.3 per cent, and 20-gram samples of each titrated in a 250-cc. Erlenmeyer at 77° F. (25° C.) with the same petroleum solvent to obtain the kauri butanol value.

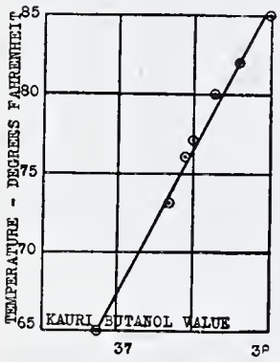

Figure 3. Effect of Temperature on Kauri Butanol Value

From the results of these titrations the graph shown in Figure 1 was obtained, which indicates that the kauri butanol value decreases in a straight-line function as the gum concentration increases.

Inasmuch as some description of the kauri test mentions an 18 per cent kauri gum content of the solution, an error from this source may be as high as 1.3 per cent.

Effect of Relative Amount of Kauri Butanol Solution Used

Eight samples containing from 17.8 to 22.5 grams of 16.6 per cent kauri butanol solution were titrated with the same petroleum lacquer diluent in the regular manner. Plotting the results produces a straight line, as is shown in Figure 2, and proves that the kauri butanol value is directly proportional to the amount of kauri solution titrated. Two laboratories using 25 cc. and 20 grams of kauri solution, respectively, should show a discrepancy in results as high as 4 per cent.

Effect of Temperature

A 20-gram sample of 16.6 per cent kauri butanol solution was titrated at 65° F. (18.3° C.) with a petroleum lacquer solvent until the end point was reached (when white paper carrying 10-point type became blurred and was no longer legible), and the result recorded. It was then allowed to warm up to 73° F. (22.8° C.), additional solvent added until the solution clouded up again, and the new reading recorded. This was repeated at 76°, 77°, 80°, 83°, and 85° (22.4°, 25°, 26.7°, 28.2°, and 29.4° C.).

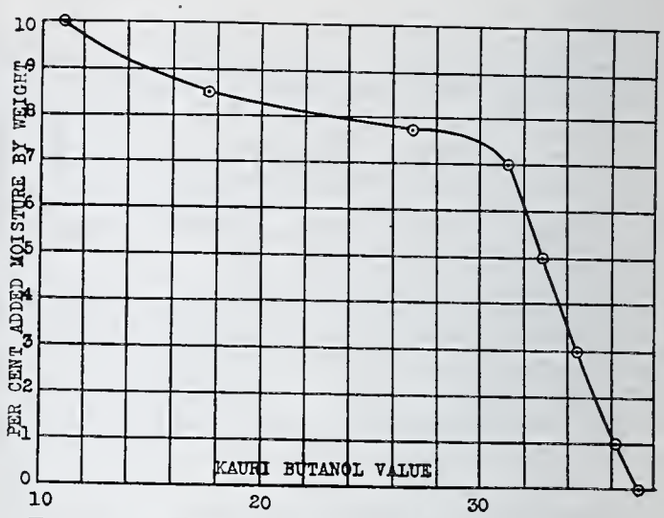

Figure 4. Effect of Moisture in Kauri Solution on Kauri Butanol Value

The plot of these results appears in Figure 3. To check these determinations, separate samples were run at 72° F. (22.2° C.) and 77° F. (25° C.) Both points fall on the line, within the limits of experimental error.

A discrepancy of 1.3 per cent in the kauri butanol numbers of a paint and lacquer solvent will result if the test is made at 68° F. (20° C.) in one instance and at 77° F. (25° C.) in another.

Effect of Moisture

Samples of kauri solution containing from 1 to 10 per cent, by weight, of added water were titrated to the regular end point with a petroleum lacquer diluent. Figure 4 shows that the amount of diluent added decreases regularly in a straight line as the water increases up to about 7 per cent, where there is a sharp break in the curve and a rapid decrease in the number of cubic centimeters which can be absorbed without clouding. Since the solubility of water in butanol is 7.3 per cent at 77° F. (25° C.), this is not unexpected.

Evaluation of Solvent Power in Terms of Toluene Value

It is clear from the above discussion of experiments that all sources of inconsistency in results of the kauri butanol test can be easily eliminated by adopting a standard procedure, with the exception of the uniformity of the basic material, the kauri gum.

Since kauri gum has been shown to be a complex mixture of varying chemical composition and physical properties, depending upon the grade of gum, it was thought that some primary standard capable of accurate reproduction should be developed. After considering several substances, toluene and *n*-heptane were selected as being most suitable. Both of these are stable substances; they may

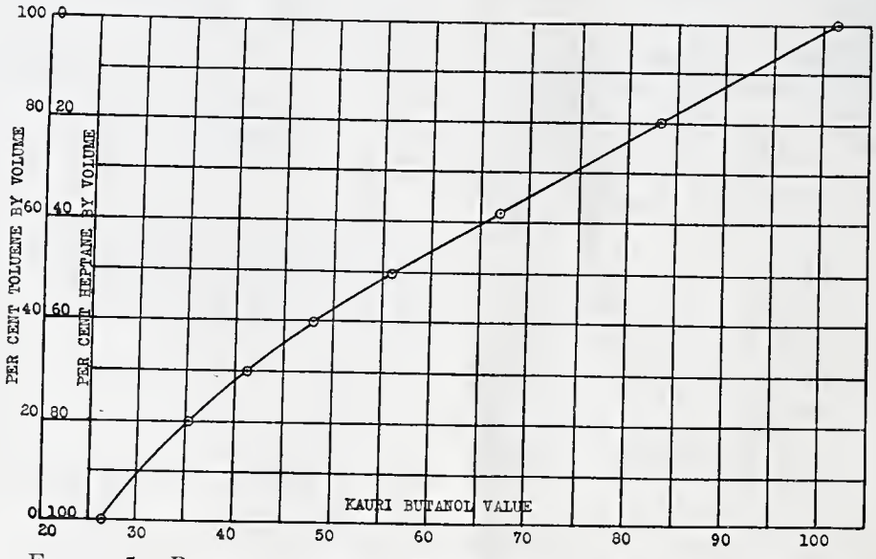

Figure 5. Relation between Toluene-Heptane Ratio (Toluene Number) and Kauri Butanol Value

be obtained easily in a C. P. state and are inexpensive enough to be used for standardization purposes. Toluene has a kauri butanol value of nearly 102 and heptane has a value of only 26; thus mixtures of these two will cover the entire range of any ordinary lacquer thinner marketed and used today. Figure 5 shows the curve for the 16.6 per cent solution of bush dial kauri gum, kauri butanol values being plotted against percentages of toluene in a toluene-heptane mixture. Once such a curve is obtained for any kauri solution, any solvent may be titrated with this solution and then expressed in terms of per cent toluene or toluene number by reference to this curve. In this way, variations due to differences in kauri solutions will be eliminated and a standard value obtained which should be easily reproducible in any laboratory, provided other points, such as the amount of kauri solution used and the temperature of test, are standardized.

The authors propose that the kauri butanol solution become a testing medium only, standardized by a primary standard, the toluene–*n*-heptane blend. The solvent power of a paint and lacquer solvent will be expressed in comparable and reproducible toluene numbers. A similar method of using a primary standard (isoöctane and *n*-heptane blend) has been adopted and successfully used by the petroleum and automotive industries for determining the antiknock value of gasolines since 1929 (*3*).

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Effect of Certain Preservatives on the Determination of Sucrose by the Invertase Method

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KJELDAHL in 1881 (*6*) proposed the use of invertase in lieu of hydrochloric acid as a hydrolytic agent of sucrose for use in the Clerget method. The first investigators to apply invertase to the determination of sucrose in food products appear to be Ling and Baker (*8*) who used the enzyme to analyze molasses and other sugar products. Invertase is replacing hydrochloric acid for the inversion of sucrose because the former is more selective, having no effect on a number of acid-hydrolyzable substances of the nonsugar group.

Since invertase is susceptible to a number of chemicals which retard or prevent its action, it was decided to investigate the effects of different food preservatives on the determination of sucrose by the invertase method. The effects of the common food preservatives, other than alcohol (*1*, *5*, *10*), on the determination of sucrose have been little investigated, although a number of studies have been conducted relating to the effects of preservatives and other chemicals upon the enzyme before it has been used as a hydrolyzing agent for sucrose, including the researches of Euler and coworkers (*2*, *3*, *4*).

Procedure

Ten-gram amounts of sucrose were weighed into 100-cc. flasks and dissolved in about 70 cc. of water, the desired amount of preservative was added, and the pH was adjusted. The invertase was added, and the volume was made up to 100 cc. The polariscope reading was taken immediately and like readings were made at stated intervals, the temperature being kept at 25° C. As each portion was removed, a small amount of alkali was added to stop the action of the invertase and to complete the mutarotation.

According to Nelson and Bloomfield (*9*) the optimum pH for the action of invertase is between 4.5 and 5. It was thought advisable to test the particular sample of invertase preparation used in this research for the optimum pH. The results are presented in Table I, which shows that the activity was fairly satisfactory for pH values from 3 to 6. The most efficient pH, however, was between values of 4 and 5.

Table I. Effect of pH on Activity of Invertase
(10 grams sucrose per 100 cc.)

Time *Min.*	pH 3	pH 3.5	pH 4.0	pH 4.5	pH 5.0	pH 6.0	pH 7.0	pH 8.0
0	38.5[a]	38.5	38.5	38.5	38.5	38.5	38.5	38.5
5	27.1	27.6	25.3	23.6	23.7	27.6	36.6	38.3
15	8.5	9.0	7.6	7.2	7.3	9.3	32.0	37.0
25	2.5	2.3	0.6	0.8	0.4	2.8	27.2	35.2
40	−1.0	−1.2	−3.1	−2.9	−2.7	−2.0	22.3	33.0
60	−4.8	−5.0	−6.1	−5.8	−5.6	−5.2	16.1	30.1
80	−7.0	−7.2	−7.6	−7.7	−7.6	−7.0	10.1	27.4
120	−9.3	−9.0	−9.4	−9.5	−9.6	−8.9	5.1	22.1
300	−10.2	−10.4	−11.1	−11.0	−11.0	−10.1	−1.0	2.1
600	−11.3	−11.2	−11.3	−11.2	−11.3	−11.3	−10.8	−6.8

[a] Polariscope readings, 200-mm. tube.

Different amounts of the various preservatives were added to sucrose solutions and the rates of inversion were determined with invertase. The pH of each solution, excepting those to which formaldehyde was added, was adjusted with acetic acid or sodium hydroxide to a value between 4.5 and 5. No alkali was added to the flasks containing formaldehyde because the preservative would have been changed; the pH value for the 0.1 per cent solution was 4.5 and for the 4 per cent solution, 3.25. The rates of hydrolysis for sugar solutions containing the various preservatives, as compared to a control containing no preservative, are given in Tables II, III, and IV.

Complete inversion did not take place with the sugar solutions containing certain preservatives. It therefore remained to be determined whether or not this retardation

was due to the action of the preservative on the rotation of the sucrose or the sugars produced by inversion.

TABLE II. EFFECT OF PRESERVATIVES ON ACTIVITY OF INVERTASE

(10 grams sucrose per 100 cc.)

Time Min.	Control	0.1 Gram[a]	0.5 Gram	1.0 Gram	2.0 Grams	3.0 Grams	4.0 Grams
			FORMALDEHYDE				
0	38.5[b]	38.5	38.5	38.5	38.5	38.5	38.5
5	25.6	25.7	28.0	28.8	29.6	30.8	32.0
15	11.2	11.8	12.4	14.2	15.6	16.2	20.8
25	1.5	2.2	3.1	4.8	9.6	10.8	16.0
40	−6.5	−6.0	−5.4	1.1	4.1	6.7	8.9
60	−9.0	−8.6	−8.4	−4.5	1.2	3.1	6.2
120	−11.4	−11.3	−9.0	−8.0	−4.6	−3.6	3.1
300	−11.2	−11.4	−10.8	−8.6	−6.8	−6.1	1.2
600	−11.4	−11.3	−11.2	−9.6	−8.1	−6.8	−4.2
			SODIUM BISULFITE				
0	38.5	38.5	38.5	38.5	38.5	38.5	38.5
5	24.8	25.0	24.6	23.8	24.5	25.0	25.2
15	10.0	10.4	10.0	9.9	10.2	9.2	9.0
25	1.2	0.9	1.0	1.2	1.0	1.8	2.1
40	−6.8	−6.5	−6.2	−6.0	−5.8	−5.2	−5.7
60	−8.8	−8.2	−8.6	−8.0	−8.2	−8.9	−9.2
120	−11.3	−11.2	−11.3	−11.5	−12.0	−13.0	−14.4
300	−11.2	−11.3	−11.5	−11.7	−12.5	−13.2	−14.4

[a] Grams per 100 cc. sugar solution.
[b] Polariscope readings, 200-mm. tube.

TABLE III. EFFECT OF PRESERVATIVES ON ACTIVITY OF INVERTASE

(10 grams sucrose per 100 cc.)

Time Min.	Control	0.25 Gram[a]	0.5 Gram	1 Gram	2 Grams	3 Grams
			BORIC ACID			
0	38.5[b]	38.5	38.5	38.5	38.5	38.5
5	28.2	27.6	28.0	27.2	28.2	30.2
15	12.1	13.0	13.4	14.0	14.8	15.2
25	2.4	2.8	3.0	4.2	9.0	10.2
40	−5.2	−5.6	−4.8	−1.6	3.0	5.8
60	−9.0	−7.8	−7.0	−3.2	0.0	1.4
120	−10.6	−9.6	−7.9	−7.8	−5.0	−2.6
300	−11.3	−10.7	−9.6	−8.6	−7.2	−5.1
600	−11.4	−11.2	−10.8	−10.4	−8.1	−5.2
			BORAX			
0	38.5	38.5	38.5	38.5	38.5	38.5
5	25.3	25.5	26.0	26.2	27.1	26.8
15	11.6	12.0	12.2	16.0	16.8	18.8
25	1.6	1.2	2.1	8.9	8.6	10.2
40	−5.0	−5.0	−4.6	2.8	4.2	6.2
60	−8.8	−7.6	−7.0	−2.8	0.6	1.7
120	−10.0	−10.2	−9.6	−6.2	−4.8	−1.4
300	−11.4	−11.2	−10.8	−9.0	−6.8	−5.2
600	−11.3	−11.3	−10.9	−9.2	−7.1	−5.4

[a] Grams per 100 cc. sugar solution.
[b] Polariscope readings, 200-mm. tube.

TABLE IV. EFFECT OF PRESERVATIVE ON ACTIVITY OF INVERTASE

(10 grams sucrose per 100 cc.)

Time Min.	Control	0.1 Gram[a]	0.5 Gram	1 Gram	2 Grams	3 Grams	4 Grams
			SODIUM SALICYLATE				
0	38.5[b]	38.5	38.5	38.5	38.5	38.5	38.5
5	24.6	25.2	24.8	24.6	25.5	26.0	25.8
15	10.6	10.8	11.0	11.6	10.8	11.4	11.6
25	1.0	1.6	0.6	1.4	0.4	1.8	2.1
40	−5.8	−6.2	−6.4	−5.9	−5.6	−6.0	−6.4
60	−9.2	−8.8	−9.4	−8.9	−9.4	−8.9	−8.4
120	−10.6	−10.4	−10.6	−10.2	−10.8	−10.4	−10.3
300	−11.4	−11.2	−11.1	−11.2	−11.4	−11.0	−10.9
600	−11.3	−11.4	−11.3	−11.4	−11.4	−11.3	−11.4
			SODIUM BENZOATE				
0	38.5	38.5	38.5	38.5	38.5	38.5	38.5
5	26.4	27.2	26.8	26.2	27.0	27.2	27.4
15	12.2	12.4	11.8	11.7	12.4	12.8	13.0
25	2.6	3.0	3.2	2.8	3.0	3.0	3.4
40	−4.2	−5.0	−3.5	−3.8	−4.3	−4.8	−4.0
60	−8.1	−7.8	−8.0	−8.2	−8.0	−8.1	−7.8
120	−10.6	−11.0	−10.8	−10.0	−9.9	−10.2	−9.0
300	−11.4	−11.4	−11.2	−11.0	−10.8	−10.4	−9.1
600	−11.3	−11.2	−11.4	−11.3	−10.7	−10.3	−9.0

[a] Grams per 100 cc. sugar solution.
[b] Polariscope reading, 200-mm. tube.

Accordingly, a series of experiments was conducted using the different sugars and the preservative without the invertase. Ten-gram amounts of sucrose and 5-gram amounts of dextrose and levulose and the maximum amounts of each preservative were separately dissolved in water and diluted up to 100 cc. After adding alkali to correct the mutarotation, readings were taken at stated intervals. The results for any solutions which caused a change in rotation are given in Table V.

TABLE V. EFFECTS OF PRESERVATIVES ON ROTATION OF SUCROSE, DEXTROSE, AND LEVULOSE

Time Min.	4 Grams of Formaldehyde[a] 10 grams of sucrose[a]	5 grams of dextrose[a]	5 grams of levulose[a]	4 Grams of Sodium Bisulfite[a] 5 grams of dextrose[a]	3 Grams of Borax[a] 5 grams of levulose[a]
0	38.5[b,c]	15.5[b,c]	−26.5[b,c]	15.5[b,c]	−26.5[b,c]
5	38.6	20.2	−27.0	16.2	−21.4
15	38.6	19.4	−26.2	13.2	−21.3
25	38.9	18.1	−25.8	12.1	−21.3
40	39.4	17.2	−25.8	11.9	−21.4
60	39.5	17.2	−25.7	11.8	−21.4
120	39.9	17.1	−25.2	11.8	−21.3
300	40.0	16.9	−25.0	11.8	−21.3
600	40.0	16.7	−25.0	11.7	−21.3
1440	40.0	16.6	−25.0	11.6	−21.4

[a] Amount of preservative and sugar in 100 cc. of solution.
[b] Readings of blank containing sugars alone.
[c] All readings in a 200-mm. tube.

Formaldehyde was the only preservative which affected the rotation of sucrose. Little effect was noted on the rotation of levulose or dextrose by this preservative. Therefore, the retardation caused by the higher percentages of formaldehyde, as shown in Table II, must have been due to the detrimental action of the formaldehyde on the invertase. The sodium benzoate and sodium salicylate had no ill effect on the rotation of any of the sugars. When invertase was present sodium benzoate seemed to slow up slightly the action of invertase in the higher percentages. Sodium bisulfite with dextrose decreased the normal rotation considerably. This would account for the increased negative rotation recorded for solutions of sucrose containing invertase and sodium bisulfite (Table II). This observation is in accord with results obtained by Tomoda and Taguchi (*12*) in work with sulfites and different sugars. Borax diminished the rotation of levulose. This in part would account for the apparent decreased activity of invertase as shown in Table III. Table III also indicates that the action of invertase was retarded by boric acid, and Table V shows that boric acid alone had no effect on the sugars tested. Therefore, the retardation was due to the effect of the preservative on the invertase. Several investigators (*7*, *11*) have found that borax decreases the rotation of dextrose and levulose, while boric acid has no effect on these sugars.

Taking into account the amount of each preservative ordinarily used in food products (usually less than 0.25 per cent), it appears that the preservatives studied would have no ill effect on the determination of sucrose by the invertase method.

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Quantitative Spectrographic Studies of Co-precipitation

II. Group II Elements with Barium Sulfate

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The co-precipitation of beryllium, magnesium, calcium, zinc, strontium, and cadmium with barium sulfate was studied spectrographically. All precipitates were prepared by the method of Popoff and Neuman, which consists essentially of the addition of the solution of the sulfate ions to the solution of the barium ions. It was found that beryllium, magnesium, and zinc do not co-precipitate, whereas calcium, strontium, and cadmium do. The type of co-precipitation has been suggested for each element.

The study of co-precipitation with barium sulfate has long been of interest and has occupied the attention of a great number of workers. Owing to the difficulty of precise determination of some of the contaminating substances by ordinary analytical methods, the authors turned to the spectrograph as a possible means of overcoming this difficulty.

Popoff, Waldbauer, and McCann (*9*) applied quantitative spectrographic methods to the study of magnesium contamination in the quantitative determination of calcium as calcium oxalate, and their method was applied to the study of co-precipitation of group II elements in the determination of sulfate as barium sulfate.

Materials

Water and sulfuric acid were purified by distillation. Sodium hydroxide, carbonate- and chloride-free, was prepared by the Cornog (*1*) method. Hydrochloric acid was prepared by dropping 12 *M* c. p. hydrochloric acid upon 18 *M* c. p. sulfuric acid. The hydrogen chloride gas formed was washed and collected in redistilled water.

All salts used were recrystallized from redistilled water to remove the very small amounts of the other alkaline earths that were initially present.

Solutions

Sulfuric acid solutions used as a source of sulfate in all the work were made up by weight from the purified stock solution which was stored in silica bottles. These solutions were made up so that 40 grams of solution were equivalent to 0.8 gram of barium sulfate, and were standardized, using weight burets, with the standard sodium hydroxide. Phenolphthalein was used as an indicator. The standard base had been analyzed using Bureau of Standards potassium acid phthalate, all necessary precautions having been taken for the exclusion of carbon dioxide during titration. Vacuum corrections were made whenever necessary. Popoff and Neuman (*8*) found that standardization against potassium acid phthalate agreed to within 0.05 per cent with standardization against benzoic acid and against constant-boiling hydrochloric acid.

Barium chloride solution containing 21 grams per liter was made up from the purified crystals.

The magnesium chloride, calcium chloride, and strontium chloride solutions used as a source of the separate cations were made up from the purified salts using redistilled water, so that 10 ml. of the stock-cation solution would contain enough cation exactly to replace all the barium in 0.8 gram of barium sulfate.

Solid beryllium chloride and cadmium iodide were added directly to the stock sulfuric acid solution when the presence of beryllium or cadmium was desired. Stock solutions of these salts as cation sources were not used because of their instability over a period of time.

The zinc chloride solution was made up using the special hydrochloric acid already described and spectroscopically pure zinc ribbon which was obtained from the New Jersey Zinc Co. Ten milliliters of this solution contained enough zinc exactly to replace all the barium in 0.8 gram of barium sulfate.

The spectographic standards were prepared by weight, using the purified salts already described. A range of standards containing from 0.05 to 1 per cent of the cation was prepared for each element. Each solution was of the same barium sulfate and concentrated sulfuric acid content as those prepared from the precipitates under examination. Some difficulty was encountered in the preparation of the cadmium standards. After the solution of the necessary amount of barium sulfate in the concentrated sulfuric acid used as a solvent, it was impossible to get the cadmium iodide into solution. It was necessary therefore to use a small amount of Kahlbaum's cadmium carbonate in order to introduce the amount of cadmium needed for the several standards.

The precipitates for spectrographic analysis were obtained from a third sample prepared under the same conditions as those for the gravimetric determinations. The precipitate was caught on a small Hirsch funnel, using a filter paper. This method was satisfactory, and eliminated the possibility of contamination from the asbestos in the Gooches, which might have occurred if the gravimetric precipitates had been used. Solutions for spectrographic analysis were obtained by dissolving 0.4 gram of the precipitate in 5 ml. of the concentrated sulfuric acid already described.

Apparatus

The apparatus for the preparation and study of the precipitates is essentially that used by Popoff and Neuman (*8*), and by Popoff, Waldbauer, and McCann (*9*).

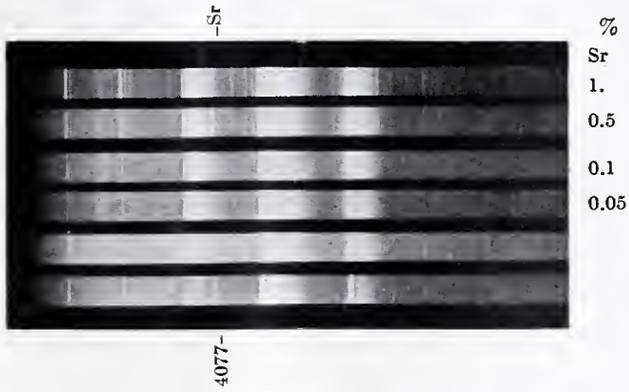

Figure 1

General Methods of Analysis

Except where otherwise stated, the following method recommended by Popoff and Neuman (*9*) was used in the preparation of the various precipitates both for gravimetric and spectrographic determination:

Approximately 40 grams of the sulfuric acid were added dropwise to an acidified (4 ml. of 6 *N* hydrochloric acid) solution containing a slight excess (5 ml.) of barium chloride, 10 ml. of the cation solution, and enough redistilled water to bring the final volume of the mixture to 350 ml. During the addition of the sulfuric acid with constant stirring, the barium solution was kept just below the boiling point by means of a hot plate. The pre-

cipitates were digested for 1 hour just below the boiling point. The mother liquor was decanted and the precipitates were washed with four 15-ml. portions of hot water and washed into the crucibles. The precipitates were heated for 1 hour at 800° C. and weighed.

For spectrographic determination, electrodes and solutions were prepared as previously described. Six drops of the solution to be analyzed, or of the standard, were placed in each electrode. The electrodes so prepared were dried in an oven at least 6 hours at a temperature of 240° to 260° C. The high temperature was necessary in order to get the electrodes completely dried, for when not entirely dry they do not burn well.

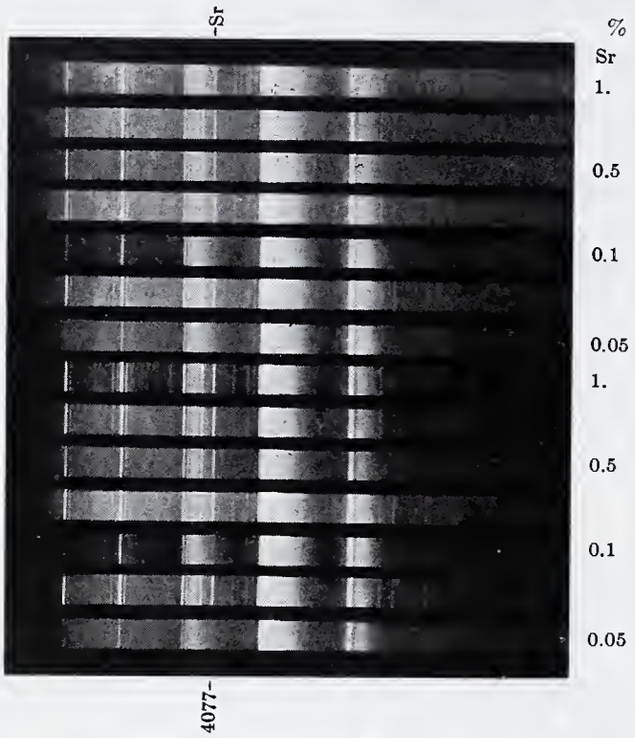

FIGURE 2

After exposure and development, final analysis of the plates was made by visual examination, using a ground-glass light-box to give a white background. Although this method is none too precise, it was felt that it gave values as reliable as the method warranted. With visual estimation, no attempt was made to extend precision beyond one figure.

This method is essentially the same as that used by Nitchie (*6*). In comparison with standards, the standards were photographed at the top of the plate followed by the spectra for analysis (Figure 1). This method is as reliable as that used by Nitchie (*6*) in which the spectra under examination were photographed between several standards (Figure 2).

The lines used in examination were as follows:

Magnesium, lines 2852, 2798, and 2790 Å.
Zinc, lines 3345.5, 3345; and 3303, 3302.6 Å.
Calcium, lines 3968.5, and 3933.7 Å.
Strontium, line 4077.8 Å.
Cadmium, lines 2288 and 2265 Å.
Beryllium, lines 2348, 3130, 3321 Å.

EXPERIMENTAL

The object of this study was to determine spectrographically the amount of co-precipitation of group II elements with barium sulfate. Of the elements in group II, radium compounds were not available, and owing to the inherent difficulties in their use no mercury compounds were studied. Beryllium, magnesium, zinc, cadmium, calcium, and strontium were studied.

The first course was to determine qualitatively whether these elements did or did not co-precipitate with barium sulfate. The precipitates were prepared from solutions containing amounts of the elements equivalent to 0.8 gram of barium sulfate. Spectrograms were taken and the presence of the element in question was determined by the presence or absence of its *raies ultimes* or most persistent lines. Pollock (*7*) states that "the absence of the residuary lines of an element conclusively proves the absence of that particular element."

Mellor (*5*) and Johnston and Adams (*4*) say that salts of the alkaline earths and magnesium are carried down by barium sulfate. But neither beryllium, magnesium, nor zinc was found to co-precipitate with barium sulfate. It would seem probable that because of the long digestion (18 hours) used by Johnston and Adams, magnesium and zinc contamination was due not to co-precipitation but to post-precipitation. Precipitates were also prepared from solutions containing double equivalents of the cation as well as by the regular method, but no co-precipitation of beryllium, magnesium, or zinc was observed.

Since beryllium, magnesium, and zinc do not co-precipitate with barium sulfate, the quantitative study was confined to calcium, strontium, and cadmium.

Precipitates were all prepared by the reverse method, having equivalent amounts of the cation present in the barium solution at the start. These precipitates were studied both gravimetrically and spectrographically and the results are recorded in Table I.

TABLE I. PRECIPITATION WITH BARIUM SULFATE

Element Studied	Barium Sulfate Calcd.	Barium Sulfate Found	Difference from Theoretical Actual	Difference from Theoretical Calcd.	Element in $BaSO_4$
	Gram	*Gram*	*Mg.*	*Mg.*	%
Calcium	0.8065	0.8036	2.9	2.23	0.2
Calcium	0.8188	0.8167	2.1	2.23	0.2
Strontium	0.7913	0.7764	14.9	14.54	1.0
Strontium	0.8066	0.7926	14.0	14.54	1.0
Cadmium	0.8215	0.8201	1.4	0.84	0.3
Cadmium	0.7997	0.7970	2.7	0.84	0.3

In column 2, the calculated weight of barium sulfate was found by the usual method from the weight of standard sulfuric acid taken; the weight in column 3 was that found experimentally by gravimetric analysis. In column 4, the actual difference was obtained by subtracting the value in column 3 from that in column 2. The value in column 5 was the change in the weight of the precipitate expected, if the per cent of the element found spectrographically were substituted for an equivalent amount of barium.

DISCUSSION

The amount of co-precipitation observed with strontium was to be expected, inasmuch as strontium sulfate and barium sulfate are isomorphous salts having the same lattice-type structure.

One might also expect a small amount of calcium to be co-precipitated according to the modified Paneth (*2*) adsorption rule: "On a polar crystal those ions experience good adsorption that form with the oppositely charged components of the lattice a compound that is poorly soluble or slightly dissociating in the solvent employed."

In the case of cadmium, a search of the literature failed to show whether or not cadmium sulfate has the same lattice-type structure as barium sulfate. Cadmium sulfate crystals belong to the orthorhombic system, as do both barium and strontium sulfates. However, a comparison of the co-precipitation of cadmium with that of strontium would lead one to believe that cadmium sulfate is not isomorphous with barium sulfate.

The low gravimetric results (compared with the amount of cadmium present), obtained when cadmium iodide was studied, are probably due to the preferential adsorption of the iodide ion and also of the CdI_4^{--} ion. According to Heym (*3*), CdI_4^{--} is formed when the slightly dissociated cadmium iodide is dissolved in water.

From a study of crystal-structure data one would not necessarily expect beryllium, magnesium, or zinc to co-precipitate with barium sulfate, and the authors were unable to detect any co-precipitation, using either the reverse or the regular methods of precipitation.

Conclusion

Calcium, strontium, and cadmium are all co-precipitated with barium sulfate.

Beryllium, magnesium, and zinc are not co-precipitated with barium sulfate.

The data for cadmium indicate the preferential adsorption of iodide ion or of CdI_4^{--}.

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Determination of Calcium in Lead-Calcium Alloys of Low Calcium Content

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THE purpose of this work was the development of a rapid, high-precision method for determining calcium in lead-calcium alloys containing from 0.02 to 0.06 per cent calcium. Small amounts of several metallic impurities were present in the alloy.

After the removal of the lead as sulfate from the nitric acid solution of the alloy, calcium and the impurities remain as the nitrates and sulfates. It is generally agreed that the best form in which to separate calcium for determination is the oxalate, and where speed is desired the volumetric evaluation of the calcium oxalate is obviously preferable to the gravimetric. Our problem was therefore that of modifying the classical method for determining calcium by the permanganate titration of the sulfuric acid solution of the oxalate, so that our requirements of precision and rapidity would be met. It was desired to run two concurrent determinations in an hour, with a precision of ±0.002 per cent calcium.

Shaw, Whittemore, and Westby (*2*), of the Western Electric Company, have published a method for this determination. They dissolve a 20-gram sample of the alloy in fuming nitric acid, add sulfuric acid, filter off the lead sulfate, and add successively ammonium hydroxide in excess, ethyl alcohol, and ammonium oxalate. The mixture is boiled for 2 minutes, and the precipitate allowed to settle for 5 minutes. The mixture is filtered through asbestos, the precipitate dissolved in sulfuric acid, and titrated hot with permanganate in the presence of the asbestos.

A careful trial of this method led us to suspect compensating errors. Repeated determinations on the same sample were generally consistent when performed on the same day and by the same analyst, but were generally inconsistent when either of these conditions did not obtain. This observation pointed to the existence of uncontrolled variables. A careful search for such variables led to the discovery of the following sources of error and experimental difficulties:

1. Incompleteness of the calcium precipitation under the prescribed conditions.
2. Difficulty in selecting end point in presence of asbestos, and possible reducing action of the asbestos.
3. Failure to make an ammonium hydroxide separation of the Second and Third Group Metals before precipitating calcium as oxalate.
4. Solubility of calcium oxalate in the unneutralized hot wash water.
5. Incomplete removal by washing of the excess ammonium oxalate in the calcium oxalate precipitate.

The experimental basis for so characterizing the above follows:

1. The Western Electric Company method specified a cooling period of 5 minutes at room temperature before filtration of the calcium oxalate precipitate. Since the completeness of the precipitation is a function of the final temperature of the solution, results obtained in summer will show a negative error from this cause measurably higher than in the case of those obtained in winter. Experiment confirmed this; microchemical examination of the filtrates from the calcium oxalate precipitation showed that cooling in an ice bath reduced the error by approximately 50 per cent.

2. The presence of asbestos in the solution being titrated was found definitely to obscure the end point, and to produce erratic results in check determinations. A positive error was introduced, caused either by a reducing action of the asbestos or by the tendency to overtitrate in turbid media, or by both. A certain alloy gave successive values of 0.051, 0.056, 0.053, and 0.055 per cent calcium by the Western Electric Company method. When the same alloy was analyzed by the method modified by the substitution of a Frittig glass filtering crucible for the asbestos Gooch, the values obtained by the same analyst were 0.040, 0.041, 0.042, and 0.042 per cent.

3. It was originally suspected that a source of error in the method lay in the failure to separate the Second and Third Group Metals as hydroxides before precipitating the calcium as oxalate. Upon investigation, however, it was proved that no measurable error was produced from this cause, at least in the case of the alloy in which we were primarily interested. This alloy contained on the average the following impurities: copper, 0.07 per cent; tin, 0.002 per cent; bismuth, 0.001 per cent; antimony, 0.001 per cent; arsenic, 0.002 per cent; and iron, 0.002 per cent. We found, however, that when the Frittig crucible was substituted for the asbestos mat, the hydroxides of these metallic impurities, if not previously removed, tended to clog the Frittig crucible and render filtration prohibitively slow. For this reason, and also to guard against samples with abnormal amounts of impurities, it seemed desirable to filter off the ammonium hydroxide precipitate before precipitating the calcium.

4. Hahn and Weiler (*1*) state that calcium oxalate is appreciably soluble in hot water, but much less so in dilute ammonia solution. In corroboration of this statement, on a

synthetic lead-calcium solution containing 0.0396 per cent calcium, we obtained a value of 0.0344 per cent on washing with hot water, and 0.0381 per cent when the washing was done with cold 1 per cent ammonium hydroxide. The last washings were proved to be free from oxalate by testing with permanganate.

5. Tests with permanganate showed that washing a calcium oxalate precipitate three times with hot water does not remove all the excess precipitant. To some extent this error compensates that given in the preceding paragraph.

It is clear from the foregoing that the Western Electric Company method, while doubtless satisfactory where speed is essential and a moderate precision sufficient, involves uncontrolled variables and compensating errors which make it unsuitable for work requiring the highest precision. We attempted to devise an improved method which would be free from those objections. The procedure follows:

Procedure

To a 20-gram sample of the finely milled and thoroughly mixed sample, contained in a 400-ml. beaker, add 100 ml. 1 to 3 nitric acid. When the vigorous reaction has ceased, heat on a hot plate to hasten solution. When solution is complete, wash the sides of the beaker with hot water and add 20 ml. 1 to 1 sulfuric acid. Remove the lead sulfate by suction filtration through an asbestos mat and wash thoroughly with hot water. Reject the precipitate. At this point the volume of the solution should be between 150 and 175 ml.

Neutralize the solution with ammonia and add 15 ml. in excess. Boil for 5 minutes and filter through a No. 42 Whatman filter or an asbestos mat, washing the precipitate with hot water. Reject the precipitate.

To the filtrate add 10 ml. concentrated ammonium hydroxide, 30 ml. of 95 per cent alcohol, and stir well. Add 2 grams of Kahlbaum's "pro-analyse" ammonium oxalate. Boil for 3 minutes. The volume of the solution should be about 300 ml. Remove from hot plate, rinse cover glass and sides of beaker with water, and allow to stand in an ice bath for 5 minutes. Temperature of solution after cooling should be 45° to 55° C. Filter the precipitated calcium oxalate on a clean Frittig glass crucible (No. 1G4), washing beaker six times with cold 1 per cent ammonium hydroxide. Wash precipitate six times with the 1 per cent ammonia solution, filling the crucible each time. Reject washings.

Remove crucible from holder, and wash holder and outside of crucible thoroughly with distilled water to insure freedom from oxalate. Replace crucible in holder and dissolve the calcium oxalate by pouring six 15-ml. portions of hot 10 per cent sulfuric acid through the crucible. Wash once with hot water after each addition of acid by filling the crucible. Add to the filtrate 20 ml. 1 to 1 sulfuric acid and dilute to 300 ml. Heat the solution to 80° to 90° C. and titrate to a faint permanent pink with 0.05 N potassium permanganate.

Notes on Procedure.

1. New Frittig crucibles should be allowed to stand overnight in dilute chromic acid mixture before being used. Crucibles should be kept in chromic acid mixture when not in use. Accumulated lead sulfate may be removed from the pores of the crucibles by washing with hot ammonium acetate solution.

2. All asbestos used should be treated with concentrated hydrochloric acid and then washed free of chlorides with distilled water.

The Constant Error

A series of experiments was performed to determine the accuracy of the method. Solutions for analysis were prepared by dissolving 20-gram samples of commercial lead, containing the impurities stated earlier in this paper, in nitric acid and adding a measured amount of standardized calcium chloride solution. The lead was obtained from the St. Joseph Smelting & Refining Company. For the preparation of the standard calcium solution, Kahlbaum's purest grade of calcium carbonate was used. A spectroscopic examination of this material showed traces of barium, strontium, and magnesium only, the total impurities being estimated at less than 0.03 per cent.

Standardization of Solutions. *Calcium Chloride Solutions.* Dry calcium carbonate was dissolved in c. p. hydrochloric acid and the solution diluted to the desired volume. The calculated calcium values of these solutions were found to agree very closely with those determined by the standard oxalate-permanganate method. Portions of the solutions (50 ml. or 100 ml.) were used for the standardization. In precipitating the calcium oxalate, the solution was allowed to digest overnight.

Standard Potassium Permanganate Solution. Merck's c. p. potassium permanganate was used in the preparation of 0.05 N solutions which were prepared and stored with the usual precautions. The solution in use was frequently standardized against Bureau of Standards sodium oxalate.

The data are summarized in Table I and show that the method invariably gives results which are in error in the sense of being too low, this error increasing somewhat as the calcium content decreases. The method is remarkably reproducible, however, as will be shown in the next section; and the existence of a constant error, if the source and magnitude of this error be certainly known, cannot be an objection. In a search for the source of the constant error, the lead sulfate and ammonium hydroxide precipitates were eliminated by spectroscopic and microchemical methods as containing negligible quantities of calcium. The filtrate from the calcium oxalate precipitate was found, however, to contain appreciable quantities of calcium. As a representative example, a synthetic solution containing the equivalent of 0.0397 per cent calcium gave an apparent calcium content of 0.0381 calcium, an error of −0.0016 per cent calcium. The filtrate from this determination was found by microchemical means to contain 0.34 mg. calcium, which is equivalent to 0.0017 per cent calcium on the 20-gram sample basis. The source of the constant error is therefore known, and cannot be eliminated without sacrifice of speed. The constant error for any given calcium content within the range covered can be obtained by interpolation from the data in Table I.

Table I. Per Cent Calcium on 20-Gram Sample Basis

Determinations	Added	Found	Average Deviation from Mean	Constant Error
	%	%	%	%
6	0.0080	0.0041	±0.0004	−0.0039
6	0.0100	0.0061	±0.0005	−0.0039
6	0.0149	0.0135	±0.0004	−0.0014
11	0.0198	0.0181	±0.0004	−0.0017
16	0.0295	0.0277	±0.0005	−0.0018
15	0.0399	0.0381	±0.0006	−0.0018
7	0.0492	0.0482	±0.0003	−0.0010
7[a]	0.0000	0.0005[a]	±0.0001	+0.0005

[a] Blank determination on a 20-gram sample of commercial lead.

In the last line in Table I are given the results of a series of blank determinations on 20-gram samples of the commercial lead. The value obtained of 0.0005 per cent calcium (0.1 ml. 0.05 N potassium permanganate) corresponds closely to the indicator error to be expected on a volume of 300 ml. in which the titration is usually made.

Precision of Method

Eight determinations were made on each of four alloys to determine the reproducibility of the method. The data are presented in Table II. Since the correction applied for the constant error was obtained by the same method, it is subject to the same accidental error. Even taking this into consideration, it is obvious from an inspection of the data in Tables I and II that the precision of the method is better than ±0.002 per cent calcium. It should be noted that this high precision is obtainable only by skilled analysts, well practiced in the method. Such an analyst can run two concurrent determinations by this method in an average time of 55 minutes, which will agree within the stated precision. This time can be reduced by about 10 minutes if the use of fuming nitric acid for the solution of the sample is not objectionable.

Table II. Reproducibility of Method

Alloy	Determinations	Average Apparent Calcium	Average Corrected Calcium	Average Deviation from Mean
		%	%	%
1	1	0.0177	0.0197	−0.0004
1	1	0.0189	0.0209	+0.0008
1	1	0.0174	0.0194	−0.0007
1	1	0.0187	0.0207	+0.0006
1	1	0.0177	0.0197	−0.0004
1	1	0.0177	0.0197	−0.0004
1	1	0.0193	0.0213	+0.0012
1	1	0.0177	0.0197	−0.0004
2	8	0.0271	0.0291	±0.0003
3	8	0.0406	0.0419	±0.0004
4	8	0.0620	....	±0.0006

We are indebted to J. D. Struthers of this laboratory for performing most of the experimental work reported.

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Silicon Tetrafluoride Volatilization

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A highly simplified apparatus, without gas-scrubbing devices, for the quantitative evolution and collection of silicon tetrafluoride gives good results since the apparatus can be thoroughly dried and possesses no dead spaces. By temperature control, the loss of fluorine caused by hydrolysis of the tetrafluoride is usually prevented and, should hydrolysis occur, the fluorine-containing products can be driven into the receiver by the application of heat to the delivery tube.

The volatilization of silicon tetrafluoride as a step in the determination of fluorine has reached its highest state of development in the thorough studies of Reynolds, Ross, and Jacob (*5*) and Shuey (*6*). These writers, together with Adolph (*1*) and Wagner and Ross (*8*), give adequate reviews of the subject. Treadwell and Koch (*7*), Wagner and Ross, and Casares (*4*) have reported the quantitative recovery of fluorine. However, Reynolds, Ross, and Jacob recovered from calcium fluoride an average of only 93.5 per cent of the calculated fluorine. Furthermore, the results of Shuey with sodium fluoride varied from 89.77 to 100.36 per cent and averaged 95.72 per cent. Willard and Winter (*9*), using a modification of the Casares procedure, obtained good recovery with inorganic fluorides but found low results on the determination of fluorine added to feed ash.

Previous workers, except Casares and others who have employed a gasometric technic, have found it necessary to scrub the silicon tetrafluoride before it entered the receiver, in order to remove substances, chiefly acids, which interfered with the analysis of the receiver contents for fluorine. Various types of wash bottles containing sulfuric acid or sulfuric acid plus silver sulfate or chromium trioxide have been used to absorb hydrochloric acid, sulfur dioxide, and oxides of nitrogen. Some observations made by this writer indicate that these wash bottles cause a loss of fluorine chiefly on account of the difficulty of drying them and their connecting tubes. An all-glass apparatus with only a trap at −35° C. between the digestion flask and the receiver also failed to give complete recovery of fluorine under various conditions of procedure. A white, frost-like sublimate formed in the top of the trap and in the bends of the connecting tubes when scrubbers were used, in spite of all precautions to eliminate water from the apparatus. This material may have been the same as the "strange deposit" first mentioned by Treadwell and Koch (*7*) in connection with their gasometric method for measuring silicon tetrafluoride. They, however, observed it only when working below atmospheric pressure. It seems likely that this deposit was silicic acid and hydrofluosilicic acid produced by the hydrolysis of silicon tetrafluoride by water retained on the glass walls or formed in the reaction bulb. The rinsings of the trap and tubes were acid in reaction, and after several determinations a white solid accumulated in the apparatus at the points where the original deposit collected. This substance was insoluble in water but dissolved in boiling alkali and was therefore probably silicic acid. In an all-glass apparatus designed to collect silicon tetrafluoride quantitatively from sodium silicofluoride decomposed by heat a similar deposit was observed, and the results of the titration of the receiver contents for hydrofluosilicic acid were low. The washings of the connecting tube of the apparatus required an additional amount of standard alkali sufficient to give a quantitative recovery of fluorine from the decomposed silicofluoride.

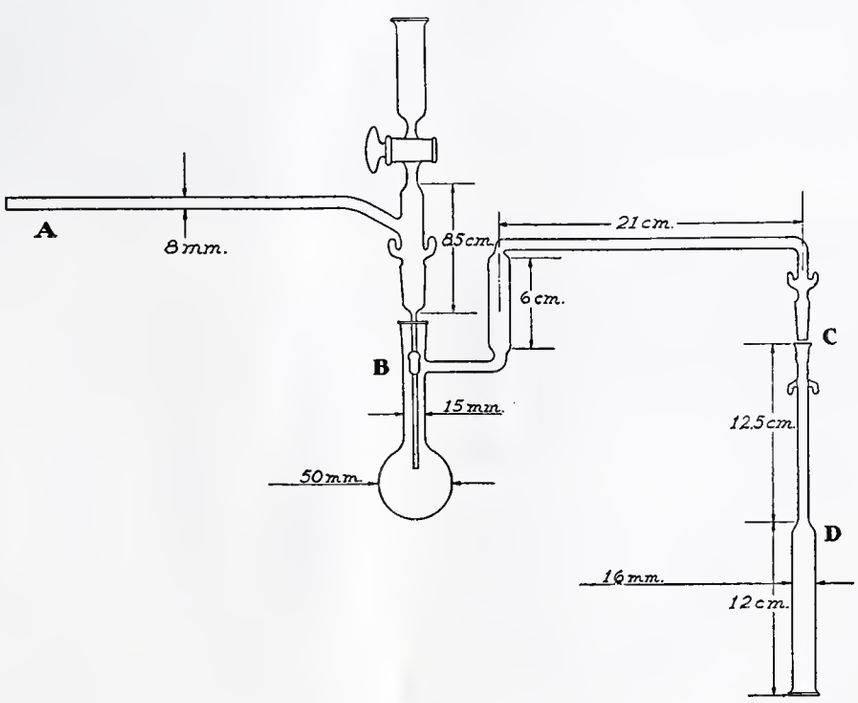

Figure 1. Silicon Tetrafluoride Evolution Apparatus

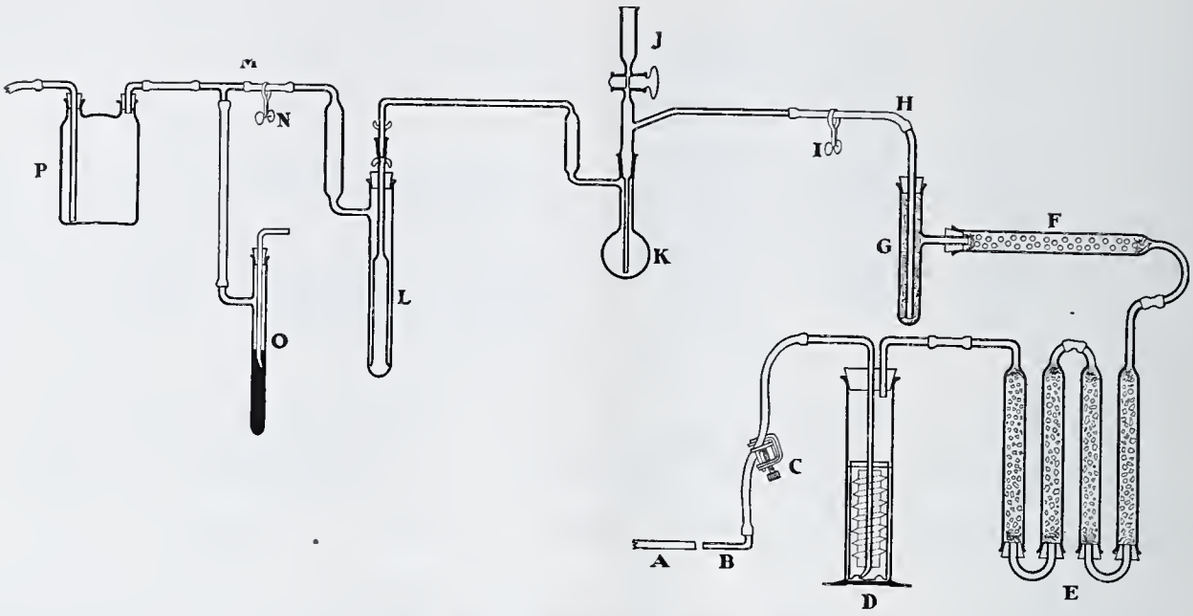

FIGURE 2. ASSEMBLED APPARATUS

In order to overcome these difficulties a highly simplified apparatus for the evolution and collection of silicon tetrafluoride was devised. The layer of water adsorbed on the glass can be removed by playing a flame over the partially assembled apparatus. A procedure was developed which usually prevented the formation of the white deposit and a method was found by which the fluorine, should the deposit form, can be driven into the receiver. This simplified apparatus required the development of the colorimetric method described in the previous paper (*2*) for the analysis of the receiver contents, since it allows substances which interfere with other fluorine analytical procedures to enter the receiver.

APPARATUS AND METHOD

The construction of the evolution apparatus is illustrated in Figure 1 in which *B* and *C* indicate ground glass joints and *D* is the adapter. In the assembled apparatus (Figure 2) *A* is a rubber tube carrying compressed air. The air-drying train consists of the Mulligan wash bottle, *D*, charged with concentrated sulfuric acid; the four 25 × 200 mm. tubes, *E*, containing calcium chloride; the tube, *F*, of the same size loosely filled with phosphorus pentoxide and glass beads; and tube *G*, which contains glass wool. *H* and *M* are rubber tubes and *L* is the receiver made from a 25 × 200 mm. test tube. *O* is a mercury-filled pressure regulating device, and *P* is a trap, the outlet tube of which is connected to a water pump. The apparatus is supported in such manner that the flask, *K*, can be shaken.

Powdered glass for use as a source of silicon is best prepared by finely pulverizing clean microscope slides. The product should be thoroughly dried and stored in a desiccator. Ordinary concentrated sulfuric acid is satisfactory and its use, instead of acids containing excess sulfur trioxide, reduces the possibility of the formation of the difficultly volatile fluorosulfuric acid and lessens the amount of acid collected in the receiver.

The procedure to be used in the evolution and collection of the silicon tetrafluoride follows:

Thoroughly dry in an oven that portion of the apparatus shown in Figure 1 and mix in the bowl of the flask the sample and 2 grams of powdered glass. If the sample is larger than a gram, use 3 grams of glass. Assemble the apparatus as shown in Figure 2, except for the adapter and receiver. Connect the air line with glass tube *B*, and during a 30-minute period blow air through the apparatus at such a rate that a steady stream of bubbles forms in the Mulligan wash bottle. From time to time heat the evolution apparatus with a flame, beginning at the end attached to *H*. This operation removes the moist air from the apparatus and the water adsorbed on the glass walls. Near the end of this period place 20 cc. of water in the receiver and insert the adapter in it as shown in Figure 2. Connect the adapter to the apparatus and change from air pressure to suction. Regulate the rate of air flow by means of screw clamp *C*, until one bubble per second forms in the receiver, and continue this rate during the remainder of the evolution procedure. Again flame the apparatus, including the ground joint on the adapter. Introduce into the digestion flask, through funnel *J*, 20 cc. of concentrated sulfuric acid, leaving a little acid in the funnel to serve as a seal. Mix the contents of the flask and heat it, by means of a paraffin bath, at 140° to 150° C. for 1.5 hours and at 175° C. for an additional 1.5 to 2.0 hours. At intervals of about 10 minutes during the evolution procedure, mix the contents of the digestion flask by shaking. If the white sublimate should form in the delivery tube, play a flame over the tube, beginning with the end near the digestion flask, until the material is entirely forced into the adapter. At the end of the procedure attach pinchcocks *N* and *I*, open the stopcock on funnel *J*, and disassemble the apparatus.

Rinse the adapter, including the silicic acid collected on its lower end, and the contents of the receiver into a flask, dilute the solution to about 200 cc., heat to boiling for 5 minutes, and add a few drops of phenolphthalein. Convert the fluorine combined as hydrofluosilicic acid in the solution to sodium fluoride by adding approximately 0.1 *N* sodium hydroxide until the alkaline color of the indicator persists on further boiling. Cool the solution in the stoppered flask and determine its fluorine content by the colorimetric method described in the previous paper (*2*). In a blank determination, 1.3 cc. of 0.1 *N* sulfuric acid collected in the receiver—an amount of sulfate which is without influence on this method. It is probable that the receiver contents could be analyzed by thorium nitrate titration procedure developed by Willard and Winter (*9*) or as modified by this writer (*3*).

TABLE I. ANALYSIS OF SODIUM FLUORIDE

No.	Sample	F Sought	F Found	F Recovered	Time and Temperature Evolution Period
	Gram	*Gram*	*Gram*	%	
1	0.0860	0.0389	0.0390	100.25	3 hrs. at 175°
2	0.1182	0.0534	0.0535	100.18	1.5 hrs. at 140–150°, 2.5 hrs. at 175°
3	0.0639	0.0289	0.0290	100.34	Same
4	0.0488	0.0220	0.0217	98.63	Same
5	0.0841	0.0380	0.0380	100.00	Same
6	0.0986	0.0446	0.0445	99.77	Same
7	0.1100	0.0498	0.0500	100.40	Same
8	0.0984	0.0445	0.0445	100.00	Same
9	0.0882	0.0399	0.0400	100.25	Same
10	0.0957	0.0432	0.0432	100.00	1 hr. at 140–150°, 1.5 hrs. at 175°
11	0.0867	0.0392	0.0392	100.00	Same
12	0.1226	0.0554	0.0555	100.18	Same
			Average	100.00	

The results presented in Table I were obtained by analyzing "Baker's C. P. Analyzed Sodium Fluoride," the same

material being used in the preparation of the standard fluorine solution required in the colorimetric procedure.

Discussion

The white sublimate collected several times in the delivery tube in analysis No. 1 and once in No. 2 in the first 1.5-hour period when the temperature was inadvertently allowed to rise considerably over 150° C. In both determinations the substance was successfully driven into the adapter by flaming the tube. In analyses 3 to 9, inclusive, very little, if any, of the material was collected; nevertheless, the tube was flamed. In analyses 10 to 12, inclusive, the sublimate did not form and the tube was not heated. It thus appears that the formation of this substance can be prevented by maintaining the temperature of the digestion flask at less than 150° C. for the first 1.5 hours of the evolution procedure and that the material can be driven into the receiver as described. It is possible that the appearance of the sublimate during the first period at temperatures above approximately 150° C. may be due to the liberation of water from sulfuric acid or its hydrate. That the substance does not accumulate during the second period in which the digestion flask is heated to 175° C. may be due to the silicon tetrafluoride having already been completely evolved.

The results given in Table II were obtained by analyzing for fluorine in the presence of certain impurities. The standard fluorine solution was prepared from synthesized sodium fluoride whose purity was checked by conversion to sodium sulfate. In analyses Nos. 4 to 7, inclusive, water collected in the delivery tube during the preliminary drying period probably because the so-called tricalcium phosphate was at least partially hydroxy-apatite, which was dehydrated by the heat. The drying period and the flaming of the tube were continued until the water was entirely expelled from the apparatus and no more collected. The white sublimate collected at least once in each of these determinations and was driven into the adapter as already described.

Table II. Analysis of Impure Fluorides

No.	Material Analyzed	CaF_2[a] Sample	F Sought	F Found	F Recovered
		Gram	*Gram*	*Gram*	%
1	CaF_2	0.1028	0.0474	0.0474	100.00
2	CaF_2	0.1049	0.0483	0.0484	100.20
3	CaF_2	0.0962	0.0443	0.0442	99.77
4	CaF_2, 0.8 g. $Ca_3(PO_4)_2$	0.1298	0.0599	0.0601	100.33
5	CaF_2, 0.9 g. $Ca_3(PO_4)_2$	0.1287	0.0593	0.0592	99.82
6	CaF_2, 0.1 g. $Ca_3(PO_4)_2$, 0.01 g. $NaNO_3$, 0.01 g. NaCl	0.0860	0.0396	0.0399	100.75
7	CaF_2, 0.1 g. $Ca_3(PO_4)_2$, 0.05 g. $NaNO_3$, 0.05 g. NaCl	0.0719	0.0330	0.0329	99.76

[a] Bureau of Standards Sample No. 79. CaF_2 content 94.83 ± 0.25%.

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Adsorption of Alcohol by Fibrous Materials[1]

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That textile fibers adsorb water and hold it rather tenaciously is common knowledge, but it does not appear to be generally recognized that other liquids may be adsorbed and held in considerable amounts even at elevated temperatures.

Analytical procedures sometimes call for the quantitative extraction of specimens placed in paper thimbles. The amount of extracted material is then obtained from the weights of the dried thimble before and after extraction. In some methods for the analysis of textiles and the purification of fibers, the final operation is to rinse or extract the specimen with alcohol or other solvent to remove nonfibrous materials and expedite drying.

The purpose of this note is to call attention to the fact that fibrous materials in the form of paper extraction thimbles, cotton, wool, silk, and rayon adsorb alcohol and hold an appreciable amount of it, even when dried to constant weight at temperatures considerably above the boiling point of alcohol. The adsorption of alcohol by silk has previously been noted and just recently a study was made of the retention of polyalcohols by cellulose (*1*, *2*).

The cotton, wool, silk, and rayon used in these experiments were carefully freed from nonfibrous materials by appropriate methods. Whatman extraction thimbles and a commercial weighted silk cloth were also used. Specimens were dried to constant weight in an air bath at 105° to 110° C. and then immersed in freshly distilled absolute ethyl alcohol at 70° C. for 15 minutes, removed, and again dried to constant weight. The increase in weight, expressed as a percentage of the weight of the oven-dried specimen—that is, the amount of alcohol adsorbed—is recorded in the table.

Fiber	Alcohol Adsorbed
	%
Cellulose:	
Viscose rayon	2.8
Cotton	1.8
Whatman extraction thimble	0.9
Silk:	
Silk fibroin	1.8
Weighted silk	0.7
Wool	1.8

When specimens containing alcohol were rinsed with boiling or even warm water, centrifuged, and dried, they returned to their original weight. When treated again with alcohol at any temperature and dried they increased in weight and on rinsing with water and drying returned to within 0.1 per cent of their original weight.

Similar experiments with diethyl ether, chloroform, carbon tetrachloride, trichloroethylene and Stoddard solvent (used in dry-cleaning) in place of alcohol did not result in an increase in weight of any of the fibers.

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Asbestos in Permanganate Titrations

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For the determination of calcium in limestone and in other silicate rocks, the usual procedure (*2, 6, 7, 8*) is to precipitate the calcium as calcium oxalate from the filtrate from which silica, iron, aluminum, and manganese have been removed. According to the procedure of the authors cited and of many others, if the calcium in the purified precipitate is to be determined volumetrically, filter paper may be used for the filtration. In order to set free the oxalate ion, the precipitate is treated with sulfuric acid, and for this purpose a concentration of acid varying from 3 *N* to 6 *N* is recommended by different authors.

The question whether or not there would be a reaction with the cellulose or other constituent of the filter paper, yielding a product oxidizable by potassium permanganate, was considered by McBride and Sherer (*5*), who dealt principally with "extracts" obtained by passing water and dilute solutions of certain reagents through the paper. Most of the results show negligible effects, corresponding to about 0.03 cc. of 0.10 *N* potassium permanganate, though in one case 0.24 cc. was used up.

The record shows no results obtained in titrations in which the permanganate took part in one of its usual oxidation reactions. Everyone must have observed the color changes that occur when a drop of permanganate is placed on dry filter paper.

Two authorities (*4, 9*) recommend that when the solution containing the oxalate is treated with permanganate, the filter paper on which the calcium oxalate was received be placed on the wall of the beaker and put into the solution near the end point.

The experiments, the results of which are shown in the tables, were carried out to test the question further. Table I shows the standardization of approximately 0.15 *N* potassium permanganate performed on different days according to approved procedure (*3*).

Table I. Standardization of Potassium Permanganate

Sodium Oxalate	Potassium Permanganate	Oxalate Equivalent
Gram	*Cc.*	*Gram*
0.3252	35.25	0.009265
0.2602	28.13	0.009250
0.2795	30.23	0.009246
0.3110	33.60	0.009256
0.2550	27.56	0.009252
	Av.	0.009254

Table II shows the effect when this standard potassium permanganate solution was used to titrate weighed portions of standard sodium oxalate, according to the same procedure, but with a piece of quantitative filter paper (Carl Schleicher and Schull-Blue Ribbon, No. 589) in the solution.

Table II. Titration in Presence of Filter Paper

Sodium Oxalate	Potassium Permanganate	Oxalate Equivalent
Gram	*Cc.*	*Gram*
0.2892	31.58	0.009158
0.2842	30.99	0.009168
0.3260	35.55	0.009170
0.3217	35.09	0.009168
0.3150	34.42	0.009178
	Av.	0.009168

Thus there appears to be a reaction, using up, on the average, 0.33 cc. of the standard potassium permanganate solution. This corresponds to an error of about ten parts per thousand, and would make a difference of 0.70 per cent in a typical limestone carrying 64 per cent of calcium as calcium oxide.

When the Gooch filter is used for separating the precipitate of calcium oxalate, the asbestos felt is usually introduced into the solution to be titrated, because suction must be used and the calcium oxalate cannot be dissolved satisfactorily on the felt, as the acid does not remain long enough in contact with it. A search of the analytical literature failed to reveal the record of any tests to determine whether or not there is any effect when oxalate is titrated by standard potassium permanganate in the presence of asbestos from an ordinary Gooch felt.

A new standard permanganate solution was prepared and standardized as above (*3*). Table III shows the standard values obtained on different days showing the stability of the solution.

Table III. Standardization of Potassium Permanganate

Sodium Oxalate	Potassium Permanganate	Oxalate Equivalent
Gram	*Cc.*	*Gram*
0.3143	38.26	0.008215
0.2955	35.98	0.008213
0.3172	38.59	0.008218
0.2653	32.29	0.008216
0.2860	34.80	0.008218
0.3174	38.60	0.008216
	Av.	0.008216

Table IV shows the titration of weighed portions of standard sodium oxalate carried out in exactly the same way, except that asbestos from a Gooch filter was added.

Table IV. Titration in Presence of Asbestos

Sodium Oxalate	Potassium Permanganate	Oxalate Equivalent
Gram	*Cc.*	*Gram*
0.2603	31.68	0.008216
0.3295	40.09	0.008219
0.2829	34.43	0.008216
0.3391	41.47	0.008217
0.3388	41.24	0.008215
0.2533	30.97	0.008216
	Av.	0.0082165

Thus it is shown that filter paper has an effect in titrations with potassium permanganate, and that asbestos has no such effect. When using filter paper, it must be added to the solution to accomplish a quantitative transfer, because some of the calcium oxalate adheres to it (*9*), while the asbestos mat, not affecting the results at all, furnishes a means of transferring the precipitate quantitatively. When using the Gooch filter, the creeping action of calcium oxalate (*1*), which may result in serious loss, is not encountered. It was found, moreover, that asbestos in suspension while stirring provided a background in the solution that made the detection of the end point easier. As a result of this work, it appears that the Gooch felt is preferable, when it is desired to determine oxalate ion by potassium permanganate.

Summary

Asbestos does not react with volumetric potassium permanganate solutions. Filter paper reacts to an appreciable extent. The presence of the asbestos is an aid in the determination of the end point.

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Estimation of Total and Bound (D) Gossypol in Cottonseed Meal

A Modified Method

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GOSSYPOL in the cottonseed is readily soluble in ethyl ether. However, probably because of the influence of heat, pressure, and moisture, when expressing the oil from the crushed seed in the commercial manufacture of the cottonseed meal, the greater part of the gossypol left in the meal becomes insoluble in ethyl ether. This insoluble part is known as bound or (D) gossypol (*1*, *2*).

The method used by Carruth (*4*) for the estimation of bound gossypol follows:

Fifty grams of meal, having been previously extracted with ethyl ether, are saturated with 100 cc. of aniline, heated for 5 minutes at 110° C., with constant stirring; then as much of the aniline as possible is removed immediately by a Büchner funnel and, after cooling sufficiently, the residue is washed with ethyl ether in order to remove the remaining aniline. The filtrate and washings are concentrated by distillation to a volume of 5 to 10 cc. The residue is washed with ethyl ether into a small beaker and allowed to stand one week in order to crystallize. The precipitate of dianiline gossypol is then filtered through a weighed Gooch crucible, and dried at 100° C. to constant weight. The dianiline gossypol is converted to gossypol by the factor 0.775.

Table I. The Estimation of Total Gossypol (Chiefly Bound) in Cottonseed Meal 1578

Carruth Method	Modified Carruth Method	Proposed Method	Recovery of Gossypol by Proposed Method[a]	
%	%	%	*Mg.*	%
0.920	0.941	1.115	19.6	98.0
0.812	0.961	1.060	19.4	97.0
0.929	0.972	1.140	18.8	94.0
...	...	1.090	19.0	95.0
...	...	1.080	19.0	95.0
...	...	1.110	19.3	96.5
...	...	1.120	..	..
Av. 0.881	0.958	1.102	19.2	95.9

[a] 20 mg. gossypol used.

From a study of the factors concerned in the determination of gossypol by a modified method (*3*), certain improvements in the method of Carruth for bound gossypol were apparent. These were a more complete removal of the gossypol from the meal; the elimination of some decomposition of probably dianiline gossypol by distilling off the excess aniline under reduced pressure, in which the greater part was distilled under 110° C. (just before completion, however, the maximum temperature of 140° C. was reached); a more complete precipitation of dianiline gossypol was also possible by the elimination of the ether used in the precipitation and washing since the precipitate is somewhat soluble in this reagent. The precipitation of dianiline gossypol was facilitated by the use of 75 cc. of petroleum ether and 10 cc. of ethylene glycol in which dianiline gossypol is quite insoluble. The precipitate was washed with petroleum ether, then with a small amount of alcohol, and finally with water. With these modifications an average of 0.958 per cent gossypol was obtained from meal 1578, compared with 0.881 per cent by the method of Carruth, or an increase of 0.077 per cent.

For the convenience of using smaller charges than 50 grams and 100 cc. of aniline the following method was worked out for total and bound gossypol. In order to obtain the total or the bound gossypol, the meal is first extracted on the Pickel extraction apparatus with petroleum ether and with ordinary ethyl ether, respectively, then dried, and stirred. All results reported in Table I are for total gossypol, inasmuch as the amount of ether-soluble gossypol in a charge of 2 grams is small, being less than 2 mg., and since the bound gossypol constitutes 90 per cent or more of the total. The accuracy of the proposed method for the determination of bound gossypol is also better shown by the determination of total gossypol, since it has been found that the amount of ether-soluble gossypol is variable, depending upon the moisture content of the meal (in press).

Modified Method in Detail

Place a charge of 2 grams, ground to pass through a 40-mesh sieve, in a medium or porous alundum filter crucible of 25 cc. capacity, extract in the Pickel apparatus 3 hours with petroleum ether in order to remove the crude oil, or 72 hours with ethyl ether for the ether-soluble gossypol in the estimation of total and bound gossypol, respectively. Dry the crucible and contents, stir the meal, and place the crucible with contents in a clean Pickel flask. Pipet (by suction) 5 cc. of aniline onto the meal. Then add 15 cc. of alcohol (90 per cent) to the flask and extract for 24 hours on the Pickel apparatus. Remove the flask, and transfer the extract to a 200-cc. Erlenmeyer flask with the aid of ethyl ether and a funnel. (The raffinose precipitated by the ether goes into solution during the process of precipitation. Any crystals of gossypol that may be adhering to the Pickel flask are transferred to a weighed Gooch crucible with the aid of water.) Remove the alcohol and ether by reduced pressure, then add 7 cc. of ethylene glycol and 10 cc. of ethyl ether to the residue. Digest on the steam bath. After the ether begins to boil, add water with shaking, at 3-minute intervals

as follows: 0.5, 0.5, 1.5, and 2.5 cc. (This procedure prevents the production of a fine precipitate which is difficult to transfer, filter, and wash.) Digest gently 15 to 20 minutes and let stand overnight. Filter through the weighed Gooch crucible, wash with alcohol (50 per cent), then with a small amount of petroleum ether, followed by 5 cc. of alcohol (95 per cent), then four times with water. Dry at 100° C. to constant weight. The factor 0.775 times the weight of dianiline gossypol gives the weight of gossypol.

The results of eight determinations on meal 1578 (Table I) average 1.102 per cent total gossypol with a maximum variation of 4.99 per cent. The recovery from 20 mg. of purified gossypol by this method is given in the last column. The average recovery is 19.2 mg., or 95.9 per cent with a variation of 4.2.

By the Carruth method, meal 1578 yielded 0.881 per cent gossypol and 0.958 per cent by the modified Carruth method, whereas the method proposed gave 1.102 per cent gossypol. The difference in results between the proposed method and the Carruth method is 0.221 per cent. Part of this difference is probably due to the gossypol remaining in the meal as it still retains a faint yellow color, and small additional amounts can be extracted from the residue from Carruth's method. After the treatment with aniline and 90 per cent alcohol on the Pickel apparatus by the proposed method, all residues are devoid of any yellow color.

Summary

A method for total and bound gossypol in cottonseed meal has been outlined which gives results of an accuracy of 95.9 per cent on known amounts of gossypol. The method is readily performed and is economical, yielding somewhat higher results than the Carruth method.

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Relation of Moisture to Extraction of Gossypol from Cottonseed Meal with Ether

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Isolated gossypol is readily soluble in anhydrous or ordinary ethyl ether. However, anhydrous ether extracts little or no gossypol from dried or air-dry cottonseed meal, whether the meal be dried with or without heat. Moisture is the important factor in extracting gossypol from cottonseed meal with ether, the highest yields occurring when the charge of meal contains about 20 per cent of water and when water is also added to the ether in the receiving flask. Meals so treated have yielded from twice to ten times more gossypol than the same samples of air-dry meal.

That swine do not thrive when fed relatively large amounts of certain cottonseed meals over a long period is ascribed to the small amounts of gossypol present in these meals. Therefore the factors affecting the estimation of gossypol are of importance.

In the usual method of estimation (*2*) gossypol is extracted from air-dry cottonseed meal with ordinary ethyl ether. Although gossypol, purified, or isolated from the seed, is readily soluble in anhydrous ethyl ether, it was found that anhydrous ether extracts materially less gossypol from moisture-free cottonseed meal.

In the quantitative estimation of gossypol, a recently published modified method (*1*) was used in which a portion of the oil was removed from charges of 75 grams of meal by washing with petroleum ether and the meal allowed to dry overnight in trays by exposure to the air. During this exposure, the meal readily absorbed or lost moisture, being responsive to the humidity of the air.

The Soxhlet apparatus was employed for the extraction of gossypol by ether. The extraction was usually continued for 48 hours, but later was extended to 72 hours because of a slightly increased yield. Both ordinary ethyl ether (not for anesthesia or medicinal use) and anhydrous ether, which was distilled over sodium, were employed.

Effect of Methods of Drying

Cottonseed meal, dried over phosphorus pentoxide at 27-inch vacuum for 2 and 6 hours at 50° C., was extracted with anhydrous and with ordinary ether. Little if any gossypol could be extracted by the anhydrous ether (an average of 0.0050 per cent), while the ordinary grade gave somewhat higher results (an average of 0.0127 per cent).

To ascertain whether the heat employed in drying the meal had rendered the gossypol unextractable, charges were dried in a desiccator over calcium chloride without any heat except that of room temperature. The results were no different from those obtained by drying with heat and vacuum.

The average amount of gossypol extracted with anhydrous ether from meals dried as above and also dried for 48 hours at room temperature in a desiccator over calcium chloride is 0.0069 per cent, compared to 0.0130 per cent with ordinary ether.

Effect of Moisture in Ether

Since ordinary ether extracted slightly more gossypol, other charges of meal dried in a vacuum oven but at 30° C. were extracted with anhydrous ether and with ether saturated with water. The results of determinations with anhydrous

ether averaged 0.0070 per cent. Results were higher (0.0414 per cent) where ether saturated with water was used, especially where more of the saturated ether was used to replace that lost during extraction (0.0471 per cent).

Anhydrous ether and ether saturated with water were also used with air-dry charges of meal 1421, with the result that the anhydrous ether gave an average yield of 0.0266 per cent, being appreciably higher than the results on the dried meals above. Air-dry meal with ether saturated with water yielded an average of 0.0468 per cent.

It was observed at this time that the charges of air-dry meal, which became damp during a rainy spell when the petroleum ether was allowed to evaporate, gave a higher yield of gossypol, an average of 0.0770 per cent.

Table I. Factors Affecting Estimation of Gossypol in Cottonseed Meal

A. Effect of Methods of Drying upon Amount of Gossypol Extracted, Meal 1421

Dried	Anhydrous ether Gossypol	Ordinary ether Gossypol
	%	%
6 hours at 50° C. over phosphorus pentoxide in vacuum oven at 27 in.	0.0000	0.0121
	0.0075	0.0133
2 hours as above	0.0076	....
48 hours at room temperature in desiccator over calcium chloride	0.0082	0.0137
	0.0112	....
Av.	0.0069	0.0130

B. Effect of Moisture in Ether upon Amount of Gossypol Extracted from Oven-Dried and Air-Dry Meal 1421

Anhydrous ether Detn.	Gossypol	Ether saturated with water by washing Detn.	Gossypol
	%		%
1[a]	0.0075	4[a]	0.0397
2[a]	0.0075	5[a]	0.0373
3[a]	0.0061	6[a]	0.0471
Av.	0.0070	Av.	0.0414
7[b]	0.0277	9[b]	0.0450
8[b]	0.0254	10[b]	0.0460
		11[b]	0.0493
Av.	0.0266	Av.	0.0468

C. Effect of Addition of Water in Receiving Flask on Amount of Gossypol Extracted (Residues of Meal 1578 after Partial Extraction of Gossypol)

Ordinary ether Detn.	Water in meal	Gossypol	Ether with 5 cc. water added Detn.	Water in meal	Gossypol
	%	%		%	%
1	20.0	0.0228	4	18.5	0.0408
2	17.6	0.0168	5	19.3	0.0463
3	17.6	0.0182	6	19.3	0.0400
Av.		0.0193		Av.	0.0424

D. Effect of Moisture in Meal and Ether upon Amount of Gossypol Extracted

Meal	Air-dry meal Detn.	Water	Gossypol	Moistened meal Detn.	Water	Gossypol
		%	%		%	%
1414	1	...	0.0059	5	26.8	0.0776
	2	...	0.0065	6	26.8	0.0843
	3	...	0.0083			
	4	...	0.0071			
		Av.	0.0070		Av.	0.0810
1412	1	...	0.0117	4	27.3	0.0285
	2	...	0.0133	5	27.3	0.0302
	3	...	0.0120			
		Av.	0.0123		Av.	0.0294
1578	1	4.9	0.0499	4	19.7	0.1237
	2	5.0	0.0485	5	19.7	0.0947[c]
	3	5.0	0.0610	6	21.4	0.1378
				7	21.4	0.1312
		Av.	0.0531		Av.	0.1309
1742	1	6.1	0.0020	4	19.3	0.0674
	2	6.1	0.0049	5	20.8	0.0785
	3	5.6	0.0061	6	20.8	0.0757
		Av.	0.0043		Av.	0.0739
1743	1	5.8	0.0002	3	21.4	0.0688
	2	5.8	0.0007	4	21.4	0.0686
		Av.	0.0005		Av.	0.0687

[a] 6 hours at 30° C. over phosphorus pentoxide in vacuum oven at 28 in.
[b] Air-dry as sampled.
[c] Omitted in average.

Effect of Water in Receiving Flask

As more gossypol was extracted with an ether saturated with water, the effect of addition of water to the receiving flask in the Soxhlet apparatus upon the amount of gossypol extracted was investigated. The charges of meal were all moistened to contain 17.6 to 20.0 per cent of water. The amounts of gossypol extracted, when water was added to the receiving flask containing the ether and to the meal, compared with those obtained without the addition of water, showed that the addition of 5 cc. of water to 350 cc. of ether in the receiving flask gave a better extraction of gossypol, averaging 0.0424 per cent compared with 0.0193 per cent with ordinary ether.

Effect of Moisture in Meal and Ether

Moisture appears to be the important factor which enables more gossypol to be extracted when water is present both in the meal and in the solvent, as well as when added to the receiving flask. Therefore, the results obtained on charges of meal conditioned or moistened with water were compared to those obtained on air-dry charges of the same meal.

In the extraction of the meal conditioned with moisture, 5 cc. of water were added to each 350 cc. of ether in the receiving flask. In the set of air-dry meals, ordinary ether was used without the addition of water.

Moisture was determined in the charges of meal immediately preceding the extraction with ether. The charges of air-dry meal were taken from samples kept in quart fruit jars, sealed with a rubber ring and cover. The meal stored in the chemical laboratory usually contained approximately 5 to 7 per cent of moisture.

The meal was conditioned for moisture by passing condensing steam slowly (5 hours) over thin layers of meal spread out in trays on shelves in an inclosed box until the meal contained approximately 20 per cent or more of moisture. The shelves were so arranged that the condensing steam circulated over each tray successively from the top to the bottom.

The data (Table I, D) show that with the addition of water to the ether in the receiving flask and also with a considerable increase in the moisture content of the meals, larger amounts of gossypol can be extracted. For meals 1414 and 1412, both containing over 25 per cent of moisture, 0.0810 and 0.0294 per cent of gossypol, respectively, were obtained. This is appreciably more than the 0.0070 and 0.0123 per cent obtained from these air-dry meals without the addition of water to the receiving flask. Thus the gossypol extracted from the conditioned meals with ether was respectively 11.6 and 2.4 times greater than for the charges of the same air-dry meals.

The influence of moisture, both in the meal and with water added to the receiving flask in contact with the ether, was shown in three other samples. Air-dry meals 1578, 1742, and 1743, containing moisture varying from 4.9 to 6.1 per cent, yielded 0.0531, 0.0043, and 0.0005 per cent of gossypol, respectively. When these meals were conditioned with moisture varying from 19.3 to 21.4 per cent, the gossypol obtained was respectively 0.1309, 0.0739, and 0.0687 per cent.

Some air-dry meals yielding little gossypol contained from 4.9 to 6.1 per cent of moisture. This is quite low. Meal held in storage during long dry spells will contain less moisture, probably comparable to those given above. For several years the authors have been unable to extract weighable amounts of gossypol from such meals.

The results show that a considerably larger amount of gossypol can be extracted when the meal is moistened with water varying from 19.3 to 27.3 per cent, and that an increased amount of gossypol can likewise be obtained from a meal containing as much as 33 per cent moisture. It is not possible to state the amount of moisture in a meal that is necessary for the best extraction of gossypol, but from 20 to 25 per cent appears to be favorable.

Discussion

Total gossypol determined in a modification of the method of Carruth (*3*) of meal 1578 was 1.102 per cent, of which free gossypol on the air-dry sample constituted 4.82 per cent; with the meal conditioned, the free gossypol constituted 11.87 per cent of the total, or an increase of 7.05 per cent due to the change in moisture content of the meal and to extraction with ether saturated with water.

Gossypol is considered to exist in cottonseed meal in two forms, free and bound, being distinguished by their difference in solubility in ether. By the process of condensing steam or merely by the addition of moisture uniformly distributed in the meal, there is a loosening of the gossypol in some manner so that it can be extracted in greater quantity by moist ether in the presence of water in the receiving flask.

The author's results indicate that there is no fixed limit between free and bound gossypol.

In the determination of free gossypol, it is essential that the moisture content of the meal immediately preceding the Soxhlet extraction be controlled and that the extraction be done by ordinary ether in the presence of about 5 cc. of water per 350 cc. of ether in the receiving flask. The presence of 20 to 25 per cent of moisture in the meal will yield appreciably more gossypol than is obtained from an air-dry meal.

The data show that the amount of gossypol obtained by extraction with ether will depend largely upon the amount of gossypol present in the meal and its moisture content at the time of extraction with ether in the presence of water in the receiving flask.

Summary

Experiments showed that little if any gossypol could be extracted from moisture-free meal by anhydrous ether, and this also held for air-dry meal. Heat, used in drying the meal, was eliminated as a cause of this difficulty. Little gossypol could be extracted from meals containing 5 to 7 per cent of moisture.

It was found that water is the important factor in the extraction of gossypol. The addition of moisture to the meal in amounts varying from 17.6 to 27.3 per cent and to the ether in the extraction flask aided the extraction, yielding increases of gossypol from twice to many times that obtained from air-dry meal with ordinary ether. Increased amounts of gossypol were obtained when water was also added to the ether in the receiving flask.

The extraction of appreciably more gossypol, with ether saturated with water from meals suitably moistened, suggests that there is no definite limit between bound and ether-extractable gossypol.

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Preparation of Permeable Extraction Thimbles for Laboratory Filtration

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The problem has arisen in this laboratory of preparing a permeable thimble to be used in a pressure Soxhlet for the hydrogenation of coal. The commercially obtainable thimbles were not the desired size nor were they of sufficient permeability. The thimbles described below were made in this laboratory with the equipment on hand.

The body used was as follows:

Monmouth stoneware clay[1]	50
Anthracite coal (−28, +35 mesh)	50

The clay is blunged with water and lawned through a 28-mesh sieve. The coal is then added and the slip blunged until a thorough mixing is achieved. The resultant slip should have a specific gravity of approximately 1.8.

The slip is drain-cast in a 2-piece plaster of Paris mold[2] until the walls are about 0.19 inch (0.47 cm.) thick.

The pieces are dried and then slowly heated in a small electric furnace with free access of air until the coal is burned out, 600° to 700° C. sufficing. The densely packed layer of clay which has settled on the outside surface during casting is then removed with sandpaper until the open structure is disclosed, after which the pieces are fired to 1050° C. The total shrinkage is about 17 per cent on the wet basis (20 per cent on the fired basis) and should be allowed for in the mold construction.

The resultant thimbles are ideal for the desired use. When 100 cc. of cold tetralin, the solvent used, were poured into a thimble of 200 cc. capacity, 2 inches (5 cm.) in diameter, 50 cc. were delivered in 1 minute. Some finely ground coal was placed in a thimble and washed several times, using alcohol to insure wetting of the coal and at the same time to prevent solution of the coal substance. The coal particles that were washed through were caught on a filter paper and their diameters measured under a microscope, using a micrometer ocular previously calibrated against a micrometer slide. The diameter of the largest particles was approximately 0.04 mm. The openings in a 325-mesh standard Tyler sieve are 0.044 mm., so the thimbles correspond favorably to 325 mesh per inch.

The permeability of the thimbles will vary approximately as the particle size of the coal used in the construction. Coal of larger particle size than that used (−28, +35 mesh) invokes difficulty in casting, while finer sizes give lower permeability.

The author's thanks are due to the staff of the Ceramics Department of The Pennsylvania State College for use of supplies and equipment in making these thimbles.

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[1] Any stoneware or good casting clay will do. Stoneware clays can be procured from The Western Stoneware Co., Monmouth, Ill.; H. C. Perrine and Sons, South Amboy, N. J., and others.

[2] For details on mold-making and casting see any elementary book on ceramics—e. g., The Potter's Craft, by Charles F. Binns. D. Van Nostrand Co., 1922, pp. 43–67 and 129–32.

Calibration and Salt Error of the Antimony Electrode

Its Application in Soil Reaction Measurements

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The calibration of the antimony electrode has been investigated with many series of buffer solutions. The buffer solutions of Clark and Lubs, and McIlvane, and the citrate mixtures of Sorensen have been found unsuitable for this calibration.

The change in slope of the antimony electrode curve as found by many workers is explained, and a new curve constructed in which the e. m. f. of the antimony electrode is a linear function of the pH from pH 3.0 to 12.0.

The antimony electrode was applied to a wide range of soils and the results were compared critically with the hydrogen-electrode figures. The salt error of the antimony electrode is defined and a new curve constructed with buffer solutions which are normal with respect to potassium chloride. The same range of soils was measured with the antimony electrode in normal potassium chloride suspension and the results compared with the hydrogen-electrode measurements.

THE urgent necessity for an electrode of more universal application than the hydrogen and quinhydrone electrodes has resulted during the last decade in investigations with electrodes of the metal–metal oxide type. The only one of these which has met with any success is the antimonious oxide electrode, which conforms more or less with the theory as discussed by Kolthoff and Hartong. Among the earliest workers in this field were Uhl and Kestranek (*20*), Kolthoff and Hartong (*11*), and Kolthoff and Furman (*10*), all of whom utilized its properties in acid-base titrations. More recently Roberts and Fenwick (*16*), Shukov and Awsejewitch (*17*), Franke and Willaman (*4*), Lava and Hemedes (*12*), Harrison and Vridhachalam (*5*), Best (*1*), Itano (*7*), and others have used it in hydrogen-ion exponent determinations in many forms and with varying technic.

In all cases a series of buffer solutions has been measured with the hydrogen electrode and the resulting pH plotted against the e. m. f. of an antimony oxide electrode when in conjunction with a standard cell. The relation between the potential of the antimony oxide electrode and the pH value was found by most of the recent workers to be a straight line from pH 1 to pH 12, but others [notably Best (*1*), Oosting (*14*), and some of the earlier workers] have shown that a change of slope occurs at varying acidities depending on the investigator.

One of the purposes of the investigation in this laboratory was to endeavor to elucidate the reason for the change in slope experienced in the use of this electrode, and also why the same behavior of the electrode was not observed by all workers. The first step was to discover if possible from the literature the type of buffer solutions used by each worker. Many of the published articles stated the type used and from others certain conclusions may be drawn. Clark and Lubs buffers were used by Best (*1*), Oosting (*14*), and also by Roberts and Fenwick (*16*). Lava and Hemedes (*12*) used potassium dihydrogen phosphate–sodium hydroxide mixtures. Franke and Willaman (*4*) do not state the type used, but as their range is from pH 1 to 12 they obviously could not have been Clark and Lubs. Harrison and Vridhachalam (*5*) calibrated their electrodes with Universal buffer solution. The majority of these investigators used rods of metallic antimony as electrodes, though Roberts and Fenwick (*16*) used crystals of antimony electrodeposited at high current density from a solution of antimony trioxide in hydrofluoric acid. Some workers added antimony trioxide to the system under examination, whereas others relied on the oxide present in the metal to give the requisite conditions.

The author used rods about 4 mm. in diameter cast from the purest antimony obtainable, and Merck's G. R. antimony trioxide. In agreement with other workers it is found that more reproducible and accurate readings are obtained with a tarnished electrode. After a long period of work in buffer solutions, however, the coating of antimony trioxide becomes so heavy as to render the electrode sluggish. It is then necessary to clean and repolish it with emery powder. After this treatment the electrode should remain standing in water for about three days to oxidize slightly; otherwise erratic potentials will be obtained. The technic adopted was that employed by Best (*1*). Measurements were made on a Cambridge Instrument Company slide wire potentiometer against a Veibel (*22*) half-cell. Quinhydrone for the standard was prepared according to the method of Valeur (*21*). A mirror-type moving-coil galvanometer was used and all readings made in conjunction with a standard Weston cell with an N. P. L. certificate. Hydrogen for the hydrogen electrode was generated from electrolytic zinc and Merck's G. R. sulfuric acid, and was purified according to Clark (*3*). The bubbling type of hydrogen electrode was used for the pH determinations.

The various buffer solutions used were as follows:

Clark and Lubs, pH 3.0 to pH 10.0
Sorensen's phosphate mixtures, pH 5.3 to pH 8.0
McIlvane's standards, pH 2.2 to pH 8.0
Kolthoff's buffers, pH 3.0 to pH 9.2
Ringer's mixtures, pH 10.9 to pH 12.0
Palitzsch's mixtures, pH 6.8 to pH 9.2
Universal buffer solution, pH 3.0 to pH 11.0

As mentioned previously, those investigators who have used stick antimony electrodes in Clark and Lubs buffers have obtained curves which change in slope at some specific pH figure. The author constructed curves at 16°, 20°, and 26° C., all hydrogen-electrode measurements being carried out in duplicate and antimony electrode measurements in triplicate. The curves obtained are of the same type as those published by Best at 14°, 20°, and 27° C. It is noticeable that in each case the relation between pH and e. m. f.

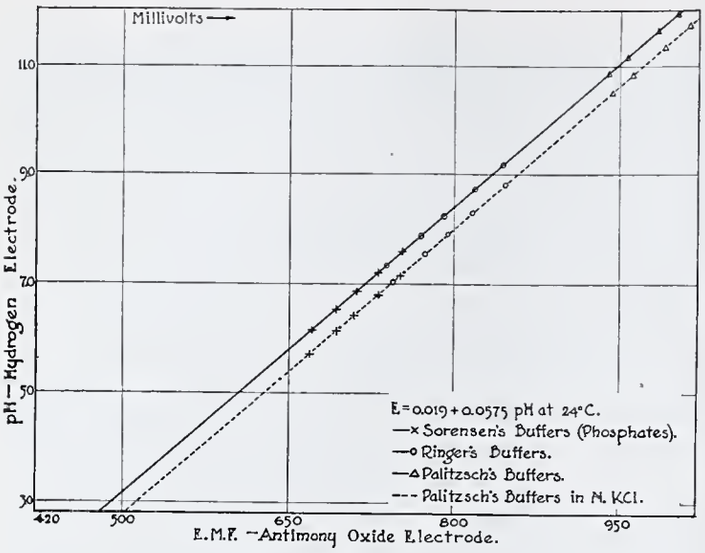

FIGURE 1

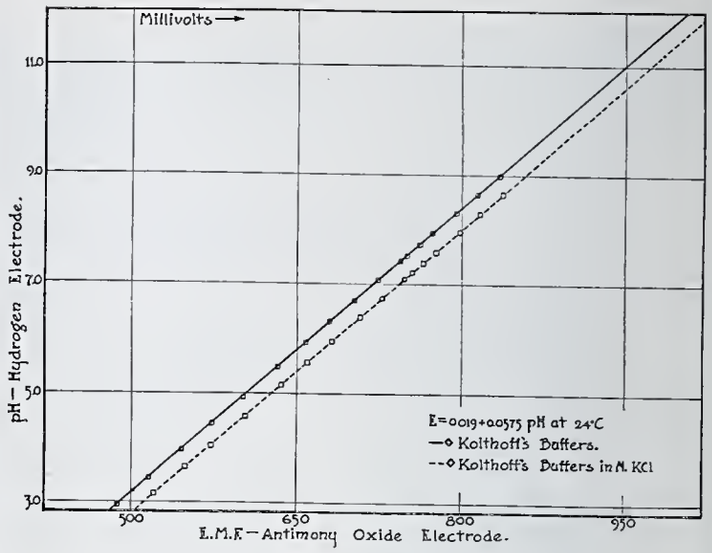

FIGURE 2

is a straight line from pH 4.0 to about pH 7.0. A change in direction takes place between the latter figure and pH 8.0, from which point it is again a straight line to pH 10.0, though of different slope from the first part of the curve. Eleven points were determined between pH 6.8 and pH 8.5 and the change is found to begin at the point where the boric acid–potassium chloride–sodium hydroxide buffers begin to operate. It had previously been pointed out, and was the experience of the author, that potassium chloride introduced a large salt error into antimony electrode determinations. It was decided as a matter of interest to eliminate potassium chloride from the series of buffers from pH 7.8 to 10.0 and to construct curves with the new solutions. Although the buffer value of the mixture would naturally be altered by this change, boric acid–sodium hydroxide mixtures are good buffers without the potassium chloride. The new determinations gave a line following on exactly from pH 7.6 where the potassium dihydrogen phosphate–sodium hydroxide buffers had left off. The cause of the change in slope was therefore shown (at least with the Clark and Lubs buffers) to be due to the potassium chloride in the final series of solutions. It has been known for some time that potassium chloride introduces a serious salt error, when pH determinations on soils are being made, though Uhl and Kestranek (*20*) stated that chlorides do not interfere in potentiometric titrations with the antimony electrode. It is therefore logical to assume that the calibration of an electrode for use in systems where appreciable concentrations of chlorides do not usually exist (e. g., soils) should be carried out in the absence of potassium chloride.

The Clark and Lubs buffer solutions were then made up as before, except that all the solutions were made normal with respect to potassium chloride. A new curve was constructed at 26° C. and was found to be a straight line from pH 4.0 to 10.0 and parallel to the line from which potassium chloride had been eliminated. The difference between the two curves was approximately 0.4 pH unit. This figure was then assumed to be the salt error of the antimony electrode with Clark and Lubs buffers.

It remained to be proved whether a curve of similar slope was obtained with the other buffer solutions, and also whether the salt error was of the same magnitude.

Sorensen's mixtures of primary and secondary phosphates have only a small range from pH 5.3 to 8.0. It is of sufficient extent, however, to cover the critical stage—viz., pH 7.5 to 8.0. Here again the antimony electrode potential was a linear function of the pH value, and the buffers normal with respect to potassium chloride also gave a parallel straight line removed by approximately 0.4 pH from those in salt-free solution. In conjunction with Sorensen's buffers Ringer's mixtures of disodium phosphate and sodium hydroxide were used to extend the curve to the region of high pH value. The range pH 10.9 to 12 connected up accurately with the Sorensen's curve both in aqueous and normal potassium chloride solution.

Kolthoff's (*9*) buffer solutions made up from succinic acid, borax, and potassium dihydrogen phosphate gave a good range of standards from pH 3.0 to 9.2. These behaved similarly to the previous buffers, giving straight parallel lines about 0.4 pH apart for the aqueous and potassium chloride solutions respectively.

McIlvane's standards consisting of disodium phosphate and citric acid were found to give entirely erroneous and very erratic results with the antimony electrode, particularly in the acid range of the buffer solutions. It is assumed for want of a better explanation that complex antimonyl citrate compounds are formed analogous with the compounds formed between antimony oxide and tartaric acid. Kolthoff and Furman (*10*) state that

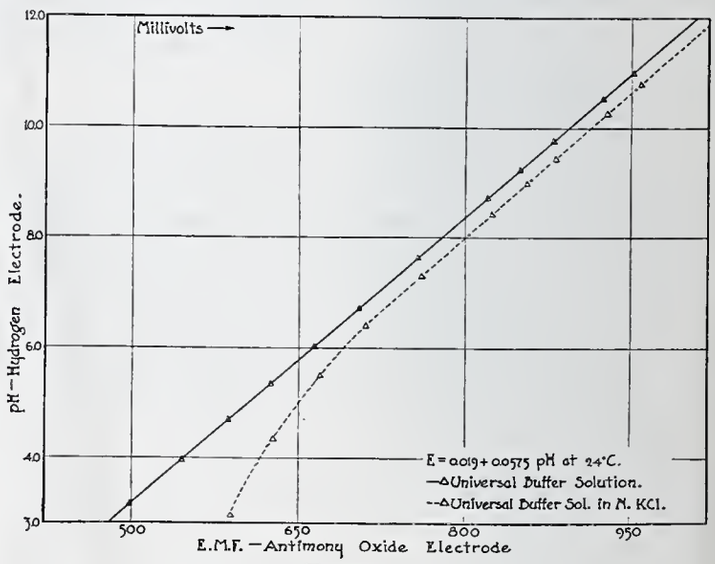

FIGURE 3

potentiometric titration of tartaric acid with the antimony electrode is inaccurate and results in measurable quantities of antimony being in solution at the end of the titration.

Sorensen's citrate–sodium hydroxide mixtures after Walbum also gave very erratic values.

Palitzsch's borax–boric acid mixtures with a range from pH 6.8 to 9.2 gave a straight line of similar slope to the preceding ones.

It was considered that, for the calibration of an electrode of this type, where salt errors are likely to occur as a result of the introduction of some specific ion, it would be better to adopt a buffer series which contained similar compounds throughout its entire range. Such a series is given by the

Universal buffer mixture of Prideaux and Ward (*15*) which, on gradual neutralization with sodium hydroxide, would subject the electrode to changes of hydrogen-ion concentration ranging from pH 3 to 12. A series of such buffers, standardized with the hydrogen electrode and measured with the antimony electrode, were found to give a straight-line graph of similar slope to that given by the previous buffer solutions. When made up normal with respect to potassium chloride, however, a curve was obtained which is illustrated in Figure 3. It was noted when standardizing the more acid solutions of this series on the hydrogen electrode that a perceptible and steady drift was occurring towards a lower potential, which seemed to imply chemical reaction in the system with consequent increase in hydrogen-ion concentration. Whatever the explanation of this phenomenon, it appears that the Universal buffer solution is unsuitable for use in normal potassium chloride. The more alkaline portion of the curve is a straight line and removed by about 0.4 pH from the normal curve.

Figures 1 and 2 show the curves obtained with the buffer solutions of Sorensen, Ringer, Palitzsch, and Kolthoff both in aqueous and normal potassium chloride solution.

Since the completion of this work there has come to hand the paper by Britton and Robinson (*2*) on the potentiometric titration of Prideaux and Ward's Universal buffer mixture with the antimony electrode, and the calibration of their electrodes with that solution. The relation obtained by them is for all practical purposes a straight line, the slight flattening of the curve above pH 11.0 being possibly due to a dilution effect, as the readings were all carried out on the same solution while adding progressive amounts of 0.2 *N* sodium hydroxide.

As all of the above buffers giving curves of the linear type were measured at 24° C., and as all agreed as to slope and deviation from the theoretical value, a single equation covers the entire series. In no case was a deviation of more than 2 millivolts from this curve noted with any buffer solution. The constants have been recalculated for purposes of comparison to apply to the chain

Sb^-/Sb_2O_3, test solution/sat. KCl/*N* KCl solution, $HgCl/Hg^+$ the equation at 24° C. being

$$E = 0.019 + 0.0575 \text{ pH}$$

or

$$\text{pH} = \frac{E - 0.019}{0.0575}$$

This equation attains more towards the theoretical value than that of other workers, the theoretical slope of which at 24° C. would be 58.9 millivolts per pH unit.

Measurements of Aqueous Soil Suspensions

The major portion of the hydrogen-ion work carried out in this laboratory is in connection with soil reaction. As the application of the antimony electrode would proceed along these lines, it was decided to examine a number of soils varying widely in distribution and reaction to test fully the applicability of the electrode. The soils used are principally of Queensland origin, though a few from New Guinea and India have been included as a matter of interest. The pH determinations were made with the bubbling hydrogen electrode, and the technic used was similar to that for the buffer solutions. Readings were taken at the half-minute period and in no case was a considerable drift experienced after this time. Soils in the alkaline range were free of appreciable amounts of carbonates. Difficulty was experienced in obtaining soils of pH greater than 8.5 with sufficiently low calcium carbonate to obviate disturbance of the carbonate equilibrium. Certain soils were therefore leached free of lime with 0.05 *N* hydrochloric acid, treated with sodium hydroxide, and the excess removed by washing with alcohol. Although not natural

Table I. Comparison of pH Values Obtained on a Range of Soils by Hydrogen and Antimony Electrodes

(pH value of aqueous and *N* KCl suspensions $\frac{\text{soil}}{\text{water}} = 1/2$)

Locality		Description		Aqueous Suspension			*N* KCl Suspension		
		Texture	Type	Hydrogen electrode	Antimony electrode	Difference H − Sb_2O_3	Hydrogen electrode	Antimony electrode	Difference H − Sb_2O_3
Beerwah	Queensland	Sand	Podsol	4.19	4.09	+0.10	3.00	2.94	+0.26
Beerwah	Queensland	Sand	Podsol	4.33	4.30	+0.03	3.62	3.67	−0.05
Samarai	Papua	Sandy loam	Alluvium	5.43	5.48	−0.05	4.37	4.38	−0.01
Scrubby Ck.	Queensland	Loam	Red loam	5.74	5.70	+0.04	4.30	4.34	−0.04
Eel Creek	Queensland	Clay loam	Red loam	6.12	6.12	0.00	4.38	4.46	−0.08
Cooran	Queensland	Loam	Podsol	6.14	6.20	−0.06	4.53	4.54	−0.01
Callagrabah	Queensland	Loam	Red loam	6.40	6.36	+0.04	4.76	4.80	−0.04
Rabaul	New Guinea	Sandy loam	Podsol	6.49	6.52	−0.03	5.07	5.10	−0.03
Cooran	Queensland	Loam	Podsol	6.50	6.54	−0.04	4.94	4.94	0.00
Markhun Valley	New Guinea	Sandy loam	Alluvium	6.54	6.49	+0.05	5.19	5.18	+0.01
Wamuran	Queensland	Loam	Podsol	6.75	6.72	+0.03	4.76	4.86	−0.10
Eel Creek	Queensland	Clay loam	Red loam	6.88	6.80	+0.08	4.90	5.06	−0.16
Byrnestown	Queensland	Sand	Podsol	6.90	6.98	−0.08	5.40	5.46	−0.06
Gympie	Queensland	Loam	Red loam	6.92	6.95	−0.03	5.27	5.26	+0.01
Scrubby Ck.	Queensland	Loam	Red loam	6.95	6.98	−0.03	4.84	4.94	−0.10
Cooran	Queensland	Loam	Podsol	7.00	7.10	−0.10	4.55	4.68	−0.13
Goomboorian	Queensland	Loam	Podsol	7.04	7.08	−0.04	5.55	5.58	−0.03
Rabaul	New Guinea	Loam	Alluvium	7.14	7.08	+0.06	5.91	5.84	+0.07
Willowburn	Queensland	Clayey sand	Podsol	7.22	7.30	−0.08	5.80	5.84	−0.04
Kin Kin	Queensland	Loam	Immature	7.24	7.25	−0.01	6.20	6.22	−0.02
Eumundi	Queensland	Loam	Podsol	7.28	7.32	−0.04	5.46	5.58	−0.12
Kilcoy	Queensland	Loam	Podsol	7.34	7.39	−0.05	5.68	5.70	−0.02
Scrubby Ck.	Queensland	Light clay	Podsol	7.39	7.36	+0.03	5.70	5.64	+0.06
Wamuran	Queensland	Loam	Red loam	7.40	7.36	+0.04	5.68	5.72	−0.04
Conondale	Queensland	Loam	Podsol	7.48	7.50	−0.02	5.97	5.96	+0.01
Scrubby Ck.	Queensland	Loam	Podsol	7.53	7.48	+0.05	5.09	5.08	+0.01
Kilcoy	Queensland	Loam	Podsol	7.74	7.78	−0.04	5.97	5.94	+0.03
Kilcoy	Queensland	Loam	Podsol	7.79	7.83	−0.04	6.20	6.03	+0.17
Wamuran	Queensland	Loam	Podsol	7.82	7.74	+0.08	6.28	6.16	+0.12
Glastonbury	Queensland	Clay	Alluvium	7.99	7.94	+0.05	5.82	5.70	+0.12
Tiruppur	India	Sandy loam	Podsol	8.08	8.12	−0.04	7.12	6.98	+0.14
Pimpama	Queensland	Loam	Podsol	8.02	8.09	−0.07	6.85	6.78	+0.07
Obi Obi	Queensland	Loam	Podsol	8.20	8.26	−0.06	6.95	6.90	+0.05
Widgee	Queensland	Clay loam	Red loam	8.25	8.28	−0.03	6.18	6.10	+0.08
Yarraman	Queensland	Loam	Red loam	8.43	8.50	−0.07	7.63	7.62	+0.01
Cunnamulla	Queensland	Heavy clay	Alluvium	8.61	8.58	+0.03	7.76	7.82	−0.06
Coulstoun Lakes	Queensland	Clay	Alluvium	8.68	8.62	+0.06	7.69	7.63	+0.06
Cunnamulla	Queensland	Heavy clay	Alluvium	8.80	8.72	+0.08	7.83	7.81	+0.02
Clermont	Queensland	Clay	Black earth	8.83	8.86	−0.03	7.80	7.76	+0.04
Blairmoor	Queensland	Clay	Brown soil	9.27	9.35	−0.08	7.70	7.64	+0.06
Blairmoor	Queensland	Clay	Brown soil	9.29	9.32	−0.03	7.70	7.63	+0.07
Cunningham	Queensland	Clay	Black earth	9.38	9.41	−0.03	8.39	8.33	+0.06
Obi Obi	Queensland	Loam	Podsol	10.46	10.56	−0.10	9.73	9.74	−0.01

The majority of the red loams classified above were not developed from basic igneous rocks, but from the highly metamorphosed schists of the coastal range.

soils, these sufficed to test the antimony electrode at a higher pH than was otherwise possible.

All determinations were carried out in triplicate, and replicates always agreed to within 1 millivolt. Antimony oxide was added to the system and the antimony electrode allowed to stand in the soil suspension. The details of technic were similar to those used in the previous buffer solution work.

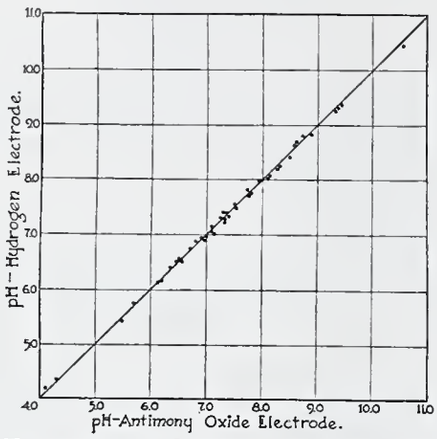

Figure 4. Correlation of pH Values Determined by the Hydrogen and Antimony Oxide Electrode in Normal Potassium Chloride Suspension

The results obtained are shown in Table I. The pH varied from 4.09 to 10.56 with the antimony electrode and the results are considered to be highly satisfactory. The average difference between hydrogen and antimony electrodes for 43 soils is less than 0.05 pH unit, the average positive deviation being 0.057 and the average negative deviation 0.049 pH unit. The maximum errors are +0.10 and −0.10. Similar results are recorded by Snyder (*18*), who used Franke and Willaman's equation.

Stirred and Unstirred Suspensions

The above results were recorded with a stationary electrode. The technic of investigators has varied considerably. Kolthoff and Furman state that agitation is necessary; Franke and Willaman and Britton and Robinson used mechanical stirrers; Roberts and Fenwick kept their solution flowing over antimony crystals; Snyder used both a rocking electrode and a stationary one; Best, and Harrison and Vridhachalam worked with unstirred suspensions; and Oosting used both stirred and unstirred soil suspensions.

It is the conclusion of the author that either method is applicable, provided that the calibration of the electrode is carried out with the same technic. For instance, Snyder obtained better results with the rocking electrode, but he was using an equation evolved by Franke and Willaman on stirred buffer solutions. The principal advantage of the stationary method is that determinations can be made in test tubes in the same way as for quinhydrone, and that the method is suitable for field determinations with a portable potentiometer of the type recommended by Itano (*8*) or Harrison and Vridhachalam.

Value of Antimony Electrode in Soil Reaction Measurements

In agricultural and research laboratories where large numbers of soils are handled daily, and in soil survey operations where reaction is an important factor in classification, a rapid method of pH determination becomes of primary importance. The time required for attainment of equilibrium with the hydrogen electrode, particularly with the Crowther electrode, usually outweighs the advantages accruing from increased accuracy of the determination. Biilman's quinhydrone electrode has therefore been adopted in most laboratories for routine work, and is eminently satisfactory with most soil types. With the growth of soil reaction work throughout the world the limitations of this electrode became apparent. Soils with a pH greater than 8.0 disturbed the quinone–hydroquinone equilibrium as a result of the acid nature of quinhydrone, and gave erroneous values. It was also pointed out as early as 1929 by McGeorge (*13*) that certain Hawaiian soils known to contain appreciable quantities of manganese dioxide gave higher pH values with the quinhydrone than with the hydrogen electrode. Heintze and Crowther (*6*) explain this as a reduction of the manganese dioxide by hydroquinone, the resulting manganese hydroxide raising the pH of the soil suspension.

Similar discrepancies have been noted with many of the basaltic red loams of Queensland, and as this soil type constitutes a fair percentage of the coastal agricultural areas, manganiferous soils attain considerable importance in daily routine work. It was with the object of applying the antimony electrode to these soils and the strongly alkaline soils of the more arid districts that the above work was carried out.

Antimony Electrode in *N* KCl Suspensions of Soils

For some years this laboratory has recorded reaction measurements of soils in both aqueous and normal potassium chloride suspensions, as recently urged by the committee on soil reaction measurements for the International Society of Soil Science (*19*). The value of this latter figure is being gradually acknowledged by soil authorities. pH values in normal potassium chloride appear to be less influenced by changes in biological and meteorological conditions and thus

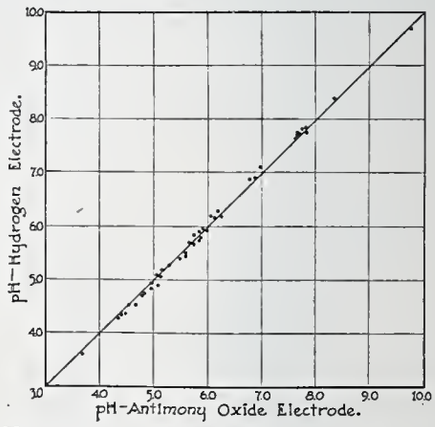

Figure 5. Correlation of pH Values Determined by the Hydrogen and Antimony Oxide Electrode in Aqueous Suspension

measure a more permanent characteristic of the soil. Worsley (*23*) discussed the effect of neutral salt solutions on Egyptian soils, and European authorities use the method widely in fertility studies. In Queensland the potassium chloride figure has been known to explain lack of fertility on sugarcane lands when the pH of the aqueous suspension failed to throw any light on the matter. It is not often with normal soils that the pH in normal potassium chloride suspension is greater than 8.5, and therefore the pH of the suspension does not prohibit the use of the quinhydrone electrode. But it is the author's experience that manganiferous soils "drift" more frequently in potassium chloride than in aqueous suspension.

It became important therefore that the antimony electrode should be applicable in salt suspension, and consequently a study of the salt error of this electrode was considered necessary. In the previous work of Best and King (unpublished)

it was found that the e. m. f. of the antimony electrode in a normal potassium chloride suspension, if read off from the calibration curve, gave a figure approximately 0.4 pH unit higher than the same suspension with the hydrogen electrode. This error was fairly constant for a large number of soils, though larger variations were occasionally experienced.

If this salt error were entirely due to a surface action on the electrode, it would be expected that the effect of normal potassium chloride on a buffer solution would be comparable with that on a soil suspension. It was decided to measure the variation in pH of a number of buffer solutions made up normal with respect to potassium chloride, and compare these with the pH of the buffers without potassium chloride. The results of this work are stated in the early part of this paper. Every series of buffers shows a difference of approximately 0.4 pH unit between the aqueous and the normal potassium chloride buffer solutions. As this figure agrees closely with the salt error experienced in measuring soils, it was thought that this second curve could be utilized for giving the relation between e. m. f. and pH for the soils in normal potassium chloride suspension.

The curve obtained for the buffers in normal potassium chloride was parallel to the original curve and removed from it by approximately 0.4 pH unit. The slope of the curve remains constant, the equation for potassium chloride suspensions reading

$$E = 0.041 + 0.0575 \text{ pH}$$

or

$$\text{pH} = \frac{E - 0.041}{0.0575}$$

In Figures 4 and 5 are shown the values for the hydrogen and antimony electrodes on the 43 soils plotted against each other, and also the theoretical line. Figure 4 refers to the aqueous suspensions and Figure 5 to the suspensions in normal potassium chloride.

The same series of 43 soils measured previously in aqueous suspension were used for this work, and the latter columns of Table I show the results obtained. The average error as compared with the hydrogen electrode is 0.058 pH unit, which is slightly larger than the error in aqueous suspension. The average positive deviation is 0.06 pH and the average negative deviation is 0.055 pH unit. These figures are considered fairly satisfactory for agricultural advisory or soil survey work where the sampling error is likely to exceed the error of the determination. For such operations the antimony electrode is strongly recommended.

It is robust in construction and does not appear to be affected by "poisons" of the type which affect the hydrogen electrode. Its range of applicability is considerable and is only limited by the pH at which antimony trioxide is soluble in the system under examination. It is proved to be a fairly reliable indicator of hydrogen-ion concentration and is accurate enough for certain avenues of soil work where extreme precision is not required. It is ideally suited for field work, particularly in the form illustrated by Harrison and Vridhachalam (*5*).

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A Multiple Steam Bath

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IN MOST laboratories use of hot-water funnels of the ordinary type is attended with inconvenience, danger, and loss of materials. The depicted copper steam-tight bath has solved these difficulties. A 6-funnel type was installed in a hood and was found to be instantly available for processes of hot filtering, drying of solids, and evaporating of liquids, and a source of heat for mild or stronger digestions.

The construction of the metal bath can be made extremely simple. Soldered joints are sufficiently strong for the covered container and 60° cones. Inlet steam and condensate outlets are made by attaching appropriate pipes to threaded locknuts soldered on to the bath. Where legs are desirable, short lengths of pipe can be screwed into additional locknuts

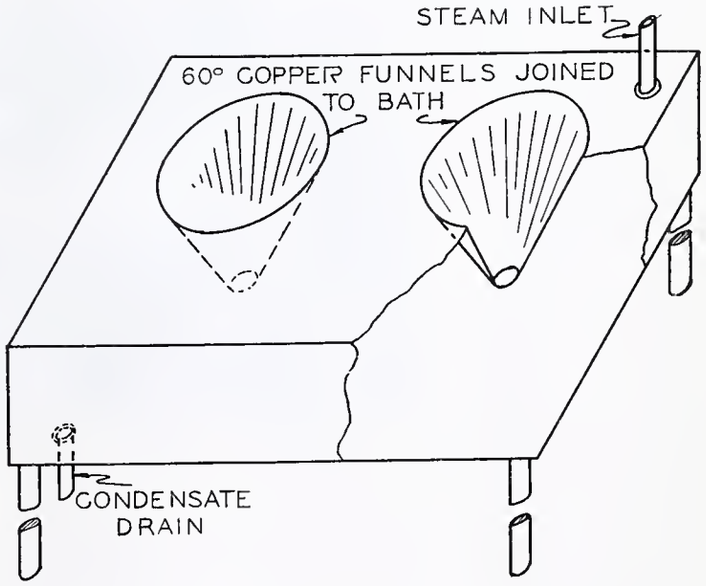

Figure 1

soldered on to the bottom of the container. The funnels may be centered or, if the bath is to be used also as a hot plate, they may be inserted asymmetrically.

Single or double funnel baths can be used as portable laboratory equipment, depending upon the usual steam can for heat.

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Tyndallmetric Examination of Filtered Liquors

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Most filtering operations are carried out for the purpose of removing suspended solid matter from the dispersion medium. While in many cases the primary object of the filtration is to dewater the solids as effectively as possible or to secure a liquid only relatively free from the dispersed phase, there are also many filtrations in which the principal objective is to remove as effectively as possible all traces of solids from the liquid medium. In both classes of filtrations the rate of flow is highly important, and numerous investigations which have been carried out from both theoretical and practical standpoints have been of great value to the filtration engineer (*1, 6, 18, 26*). However, relatively little work has been reported on the effectiveness of filtration as determined by the quality of the filtrate. This latter is of the utmost importance in the numerous types of filtrations carried out primarily to obtain a high degree of purification or the nearly complete removal of solids and colloidal matter from the liquid.

The effectiveness of a filtration as determined by the extent to which suspended solids have been removed is judged ordinarily and most readily by the appearance of the filtrate, which may be described as turbid, cloudy, hazy, clear, brilliant, sparkling, etc. More precise evaluation has been impossible in most cases because of the lack of suitable test methods and instruments for examining filtrates. Nephelometric and turbidimetric methods have been fairly satisfactory only for comparatively cloudy filtrates and for unfiltered liquids (*8–16*). Very clear or brilliant filtrates on the other hand have offered great difficulties and most measurements have been made by comparison methods which are essentially qualitative in nature and which depend to a large extent upon the opinions and the judgments of the individual operators. For the examination and comparisons of very "clean" filtrates advantage must be taken of the Tyndall beam principle in order to show up the minute turbidities present. Tyndall beam measurements have been made in a quantitative manner for a number of dispersed systems (*1–5, 7, 17, 19–24, 25, 27–33*). None of the methods or apparatus described, however, has been particularly suitable for the clarity examination of highly clarified liquid media.

This paper is a preliminary report on an apparatus and a method developed specifically for the quantitative examination of filtered or highly clarified liquids. Because of the small amount of turbidity in such liquids, the great variation in their character, the presence of color, and especially because of the necessity for the precise determination of small differences, this problem has presented considerable difficulty. The method and apparatus as developed have been useful in both theoretical and practical investigations on filtration, in the solution of specific filtration problems, and in the evaluation of filter aids and their effect on filtration.

An objective of the study has been to provide an apparatus of high accuracy and yet one sufficiently simple and inexpensive to be suitable for use at filter-press stations as well as in the laboratory. Further investigations are now in progress, intended to make further improvements of the apparatus, and include studies of a wide range of industrial filtrations.

Description of Apparatus

The principle of the method is to measure photometrically the intensity of the Tyndall beam produced in the filtrate by passing into it, under standard conditions, a controlled and constant light beam. The turbidity or clarity is expressed directly in photometric units.

The apparatus consists essentially of a constant primary light source, an appropriate optical system for the incident beam, a suitable mounting for the cell containing the liquid, an optical system for the examination of the Tyndall beam, and an appropriate photometric measuring system, which may provide for the direct comparison of the Tyndall beam with a secondary standard light source, with a split beam from the primary light source, or by the use of the photoelectric cell or the photographic plate. In the apparatus described, the first method has been used. The Macbeth illuminometer (Leeds and Northrup Company) has been satisfactory for most purposes and is shown here as one of the simplest and least expensive set-ups tried (Figure 1).

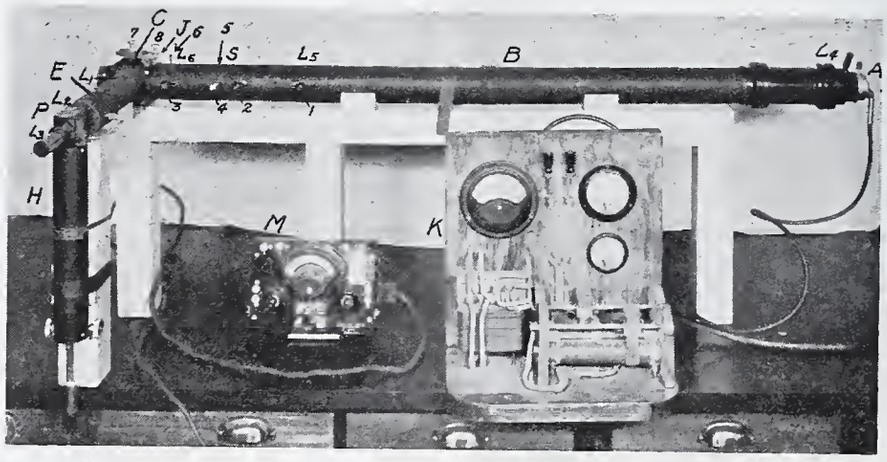

Figure 1. General View of Photometric Tyndallmeter

The cell containing the liquid to be examined is placed in a holder indicated at *C*, suspended from an accurate mechanical stage which permits the movement of the cell in two directions (parallel and at 90° to the path of the incident light beam). The exact position of the cell is read by vernier scales. The cell is of plane-surfaced optical glass.

The tube *B* houses the optical system for the incident light beam. *A*, the primary light source, is a 6-volt, 5-ampere concentrated filament lamp, mounted in such a manner as to be centered accurately by means of three set screws. It may also be focused and clamped securely in position when the proper focus is secured. For maintaining a constant light intensity from this bulb a strictly uniform current must be supplied to the filament. This is provided from ordinary 110-volt alternating current by means of the control panel *K* which is provided with a transformer, variable resistances, ballast tube, and suitable voltmeters and ammeters. Satisfactory constant current can be secured also from fully charged storage batteries of large capacity.

The incident beam optical system consists of lens L_4, lens L_5, slit *S*, and lens L_6. The latter two lenses and the slit may be focused by adjustments in their positions, as indicated by knobs

1, 2, and 3. The width of the slit opening is also adjustable in a vertical position by knobs 4 and 5 located on opposite sides of tube B. The incident light beam is aligned with the axis of the emergent beam optical system by means of knob 6.

The emergent or Tyndall light beam system is housed in tube E and in the Macbeth illuminometer head. Lenses L_1 and L_2 are located in E as indicated. The Lummer-Brodhun photometric cube is located at P and lens L_3 is located in the telescope supplied with the Macbeth instrument. The Macbeth illuminometer H consists of the head containing the photometric cube, the telescope for viewing the illuminated fields to be matched, and a tube that contains a diaphragmed carriage in which is mounted a small bulb which is the comparison light source. The position of the lamp carriage is adjustable by a rack and pinion upon which is engraved a direct reading scale calibrated in foot-candles. The intensity of the comparison light is therefore controlled by the distance of the bulb from the photometric cube, the scale following the inverse square law. The comparison lamp is standardized by reference to a standard light source. The control instrument for the Macbeth reference lamp is shown as M.

In operation the emergent Tyndall beam from the liquid under examination is projected and uniformly distributed over the inner circle of the Lummer-Brodhun cube. The outer circle is illuminated by the reference light of the Macbeth instrument. The intensity of the outer circle is adjusted to match the intensity of the inner circle and the value of the intensity of the emergent beam is read directly from the calibrated scale. Photometric matches are readily obtained and can be checked with accuracy by various operators. Provision is made for measuring wide variations in intensity by the use of calibrated neutral screens and for the matching of colored light by the use of suitably selected color screens.

Elementary Optics of Apparatus

The image of the filament F is focused by the double lens combination L_4 in the plane of the entrance pupil of lens L_5. In the plane of the exit pupil of lens L_5 all the light from the filament is collected in a small circle and all the rays from any point on the filament are traveling parallel. This forms a uniform circle of light of maximum intensity and the slit S is placed therefore to coincide with this circle. Lens L_6 projects a reduced image of this intensely illuminated slit in the cell C containing the liquor.

The emergent Tyndall light from the cell is collected by lens L_1 and imaged in the plane I_0 ($A'B'$). A diaphragm is inserted at this point to block out all light from the Tyndall beam except for a 2-mm. circle at the center of focus of the incident beam. The diaphragm indicated by the dotted line is inserted in the plane of the Tyndall beam image $A'B'$. As this image is equal in size to the Tyndall beam itself, a 2-mm. diaphragm in the plane $A'B'$ is equivalent to an imaginary diaphragm of 2-mm. opening placed in the plane of the Tyndall beam. Lens L_2 is located the distance of one focal length from plane I_0 and its exit pupil lies slightly more than one focal length to the rear—that is, in the plane I_L. In this plane the light from the Tyndall beam is focused as a uniformly illuminated circle. The plane of the inner circle of the photometer cube P is therefore in the plane of I_L.

The inner and outer circles of cube P are viewed by lens L_3 placed at one focal length from plane I_L. At the exit pupil, one focal length behind lens L_3, all rays from each point on the two circles are parallel, and the lens of the eye placed in this plane adjusts itself for parallel light and focuses the two circles on the retina.

In the plane of the photometer cube I_L, uniformity of illumination is obtained simultaneously in two ways. First, the image of the Tyndall beam which is not uniformly intense over its surface is focused by lens L_2 at infinity; therefore, in the plane I_L, all rays from each point in the Tyndall beam are parallel and the resultant image in this plane is a uniform circle of light. Second, lens L_2 focuses in the plane I_L, an image of lens L_1 which is a uniformly illuminated surface as shown in Figure 2.

By studying the course of the rays in Figure 2, the method of obtaining this double uniformity of illumination is clearly demonstrated. The line AB represents the size of the Tyndall beam covered by lens L_1. The two rays 1, 1 proceed from point A to points a and b, the opposite sides of lens L_1. Likewise, the two rays 2, 2 proceed from B to points a and b. Stated in another way, the light which emanates from point A and which lies within the angle formed by rays 1, 1 is uniformly distributed over the lens L_1 and the light which emanates from the point B and which lies within the angle formed by rays 2, 2 is also uniformly distributed over lens L_1. It follows that light which emanates from all points between A and B also fills lens L_1 uniformly. Therefore, as the intensity of illumination at each point on lens L_1 is a resultant of the light from all points between A and B, the intensity at all points on lens L_1 will be equal, no matter how much the light varies in intensity from point to point between A and B, and therefore lens L_1 is uniformly filled with light.

Rays 1, 1 proceed from lens L_1 as rays 1_a, 1_b and are united at point A' in the plane I_0, to form an image of A. Rays 2, 2 proceed from lens L_1 as rays 2_a, 2_b and are united at point B', in the plane I_0. Lens L_1 is placed at twice its focal length from the Tyndall beam and therefore the image plane I_0 is at twice the focal length on the other side of lens L_1 and the image $A'B'$ is equal in size to AB.

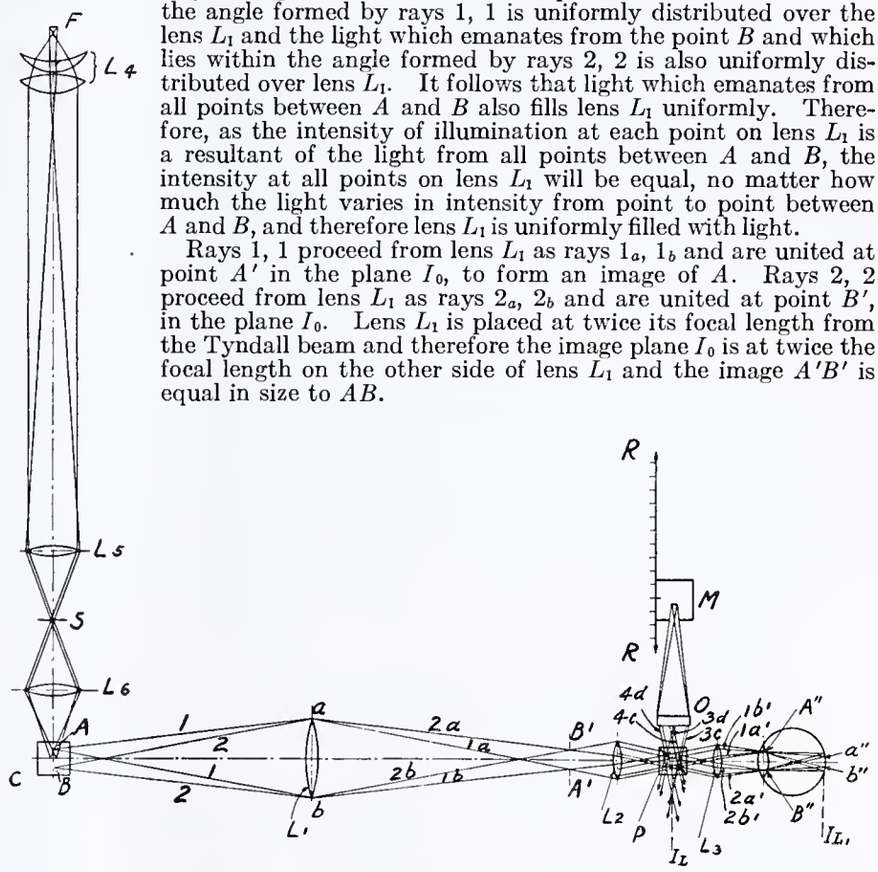

Figure 2. Optical Diagram of Tyndallmeter

Rays 1_a and 1_b proceed from A' to lens L_2 and from there they are projected parallel. Rays 2_a and 2_b proceed from B' to lens L_2 and from there are projected parallel. The parallel rays 1_a and 1_b intersect the parallel rays 2_a and 2_b in the plane I_L, ray 1_a intersects ray 2_a at a' and ray 1_b intersects ray 2_b at b'. This establishes the two conditions for uniformity of illumination of the image $a'b'$. First, as the rays from point A' and from point B' and consequently from all other points on $A'B'$ are traveling as parallel bundles, and as each parallel bundle covers the image $a'b'$, the latter must be uniformly illuminated. Second, the rays 1_a, 2_a proceeding from point a on lens L_1 intersect at a' to form an image of a; the rays 1_b, 2_b proceeding from point b on lens L_1 intersect at b' to form an image of b; consequently, a uniformly illuminated image $a'b'$ is formed of the uniformly illuminated lens surface ab.

Rays $1_{a'}$, $1_{b'}$ continue traveling parallel to lens L_3 and are therefore focused in the rear focal plane of L_3 at the point A''. Similarly, rays $2_{a'}$, $2_{b'}$ are focused at the point B''. Therefore, in the plane I_0' an image $A''B''$ of the image $A'B'$ is formed. This image is in the plane of the lens of the eye. At the same time from lens L_3 to the plane $I_{0'}$ rays $1_{a'}$ and $2_{a'}$ are traveling parallel and rays $1_{b'}$ and $2_{b'}$ are traveling parallel. Therefore, as the lens of the eye is focused for parallel light, rays $1_{a'}$ and $2_{a'}$ are united on the retina (plane I_{L1}) at the point a'' and rays $1_{b'}$ and $2_{b'}$ are united at the point b''. Therefore, the retina receives a focused image of the uniformly illuminated inner circle of the photometer cube.

The optics of the comparison beam light is much the same as that of the emergent beam. The principal parts of the illuminometer H (Figure 1) consist of the movable light M attached to the scale RR and the ground glasses O (Figure 2). The intensity of light emanating from the ground glasses is varied by moving the light M, the degree of intensity being read on scale RR.

The ground glasses O scatter the light rather uniformly in all directions and thus illuminate the reflecting surface in photometer cube P. For simplicity, parallel bundles 4_c, 4_d and 3_c, 3_d are shown emanating from the ground glasses O. As lens L_3 is adjusted for infinity focus, these rays are imaged in the pupil of the eye $A''B''$ as image 3, 4. At the same time, the c rays and d

rays are each traveling parallel. Therefore, the lens of the eye images *cd* on the retina as a ring of light surrounding the circle of light from the emergent beam.

Application of Apparatus

Clarity examinations of filtered liquids can be made with the apparatus described with both speed and accuracy. When the apparatus is in adjustment, determinations can be completed within an average of 2 minutes. The apparatus is highly sensitive, however, and care must be taken to have the cells and optical parts scrupulously clean when examinations are made in which small differences are significant. Examples are given below for a number of widely different types of filtration. In some of the examples the differences are considerable and the turbidities high, thus permitting relatively easy readings. In others the differences and turbidities are small,

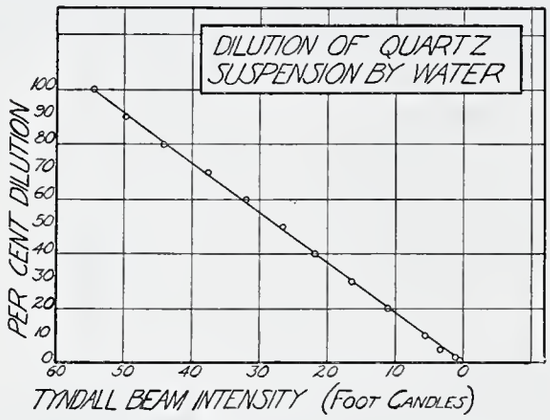

Figure 3

calling for refined work. It is for accurately measuring small differences in these low turbidities that the apparatus was specifically developed.

Clarification of Water

The use of the apparatus is shown by reference to a relatively simple type of clarification—i. e., in water purification. Comparisons are given in Table I for the turbidities of water purified by conventional methods.

Table I. Clarification of Water

	Description of Sample	Intensity of Tyndall Beam *Foot-candles*
1	Untreated tap water, Manville, N. J.	2.55
2	Same, after filtration through Berkefeld filter	0.70
3	Same, after filtration through quantitative filter paper	1.15
4	Same, after treatment with alum and filtration through paper	0.57

High Tyndall beam intensities indicate greater turbidity. Within limits and for practical purposes the degree of clarification is inversely proportional to the intensity of the Tyndall beam. In making comparisons of this kind it is, of course, necessary to confine comparisons to liquors of the same general character.

The results show that filtration through rigid, porous filters is highly effective, but that alum treatment is superior. Manville tap water is representative of average domestic water. Readings as above are accurate to 0.05 foot-candles.

Clarification of Varnish

In the manufacture of high-quality varnish, clarification is necessary to secure the final "polish" or clarity desired. This clarification may be effected by the use of centrifugals or by pressure filtrations. A sample of good quality varnish was clarified by various means and examinations of the clarified varnish were made with the clarity apparatus. The results are shown in Table II.

Table II. Clarification of Varnish

	Description of Sample	Intensity of Tyndall Beam *Foot-candles*
1	Original varnish unclarified	166
2	Same, clarified by centrifuge (2500 r. p. m., 30 min.)	151
3	Same, gravity filtration with paper	109
4	Same, vacuum filtration with triple thickness of paper	97
5	Same, pressure filtration with diatomaceous filter aid	60

Filtration of Beef Extract

The clarification of biological extracts and preparations is a very difficult problem because of the type of impurities present. Table III gives the results of removing suspended material from beef extract by various methods.

Table III. Clarification of Beef Extract

	Description of Samples	Intensity of Tyndall Beam *Foot-candles*
1	Unfiltered beef extract	262
2	Filtered through two layers of flannel cloth	219
3	Filtered through alundum crucible	190
4	Filtered through cotton plug	122
5	Filtered through diatomaceous filter aid	39

The above methods of removing suspended material show that greatly varying degrees of clarification are obtained by various means and that these differences can be measured tyndallmetrically. The clarification secured by the filter aid filtration is obviously superior.

Miscellaneous Filtrations

A number of other industrial filtrates are listed as a miscellaneous group and show interesting differences. The amounts of turbidity present in these materials vary considerably, as shown by the tyndallmetric data. At the start of a filtration cycle the degree of clarification is usually poor as compared with the final results; yet even at the start there is a very marked decrease in dispersed particles as shown by the Tyndall beam intensity of early fractions of filtrate as compared with the original liquors. The filtrates reported in Table IV were obtained from pressure filter press operations using Celite filter aids.

Table IV. Miscellaneous Industrial Filtrations

(Tyndallmetric readings expressed as foot-candles)

Kind of Material	Before Filtration	Start of Cycle	End of Hour Cycle
Glue	670	60	10.0
Wine	162	40	5.0
Beer	114	30	6.0
Pectin	105	76	50.0
Coffee extract	440	40	6.0
Dry cleaner's solvent	8.7	3.9	2.6

The samples of wine, glue, beer, and coffee extract examined exhibited very prominent Tyndall effects and after the start of the filtration cycle dropped to approximately the same clarification value. This would indicate that the easily removable suspended colloidal impurities are removed almost immediately, leaving the extremely small suspended particles to build up in the interstices of the filter cake and form a more impervious and effective filtering medium. This is shown by comparing the data at the beginning and at the end of the filtration cycles. In all cases except pectin, the degree of clarification at the end of the cycle is greatly improved.

Accuracy of Apparatus and Method

The accuracy of the apparatus is shown by a series of tests made with a quartz suspension. (Figure 3) The quartz suspension was made by dispersing finely ground quartz in water. Then by settling and decantation, a fraction was secured containing only particles smaller than 0.25 micron in size. This fine dispersion was then diluted with turbidity-

free water to give a series of dispersions containing definite and systematically varying amounts of particles, the size of which was the same for all dispersions. The results show that the Tyndall beam intensity is a direct function of the concentration of particles (number of particles per unit volume).

Applications of Clarity Measurements to Cane-Sugar Refining Industry

In the refining of raw sugar the importance of the filter station in the refining process is fully recognized. Melted raw sugar is difficult and expensive to filter and most refineries in this country now depend entirely upon diatomaceous filter aids for the clarification of their sugar liquors. Special grades of these filter aids have been developed to meet particular requirements. The degree of clarity of filtered raw sugar liquors is highly important, as small differences in clarity show up strikingly in all subsequent refining steps, particularly in bone-char decolorization, in evaporating, in crystallizing, in the final recoveries obtained, and in the quality of the refined sugar. Up to the present there have been no methods of clarity evaluation available to the sugar industry that have met adequately the requirements of sensitivity and accuracy. As the apparatus described has been developed principally for use in the sugar industry, some examples of its use in the solution of practical problems will be given.

The differences between the degrees of clarity obtained with different filter aids and with a given raw sugar are shown in Table V. Similar figures are given for the count of colloidal particles as measured by an ultra-microscopic method recently developed at the Johns-Manville Research Laboratories. This method will be described in a subsequent paper.

Table V. Examination of 60° Brix Raw Sugar Filtrates (15–30 Min. Fractions)

Liquor Examined	Rate of Flow		Amount of Filter Aid Used	Particle Count	Clarity Expressed as Tyndall Beam Intensity
	Gals./sq. ft./hr.	*Liters/sq. meter/hr.*	*%*	*Number/cc. × 10¹⁰*	*Foot-candles*
Unfiltered raw sugar	..	....	..	143.0	16.2
Filtered with filter aid 1	5.8	236.4	0.38	7.7	0.65
Filtered with filter aid 2	14.1	574.5	0.38	16.3	1.08
Filtered with filter aid 3	36.3	1478.9	0.38	57.7	1.65

The results show an interesting and consistent relationship between the number of colloidal particles unremoved by filtration and the Tyndall beam intensities of the filtrates. The differences noted between the filtrates from the three filter aids tested are highly significant in sugar practice. Such differences show the degree of refinement necessary in this measurement. The clarity figures have been found to be better criteria of liquor quality to the refiner than the particle counts. Apparently the over-all optical effect as measured by the Tyndall beam intensity is an index of those colloidal impurities which are most troublesome in refining and which are effectively removed only by a very efficient filtration.

Small clarity differences are known to occur throughout the course of a filtration cycle, the clarity ordinarily improving regularly as the filter cake builds up.

Table VI shows this change of clarity with the length of cycle for the three filter aids with three different raw sugars. Particle counts are again given for reference.

These results were obtained in a laboratory filtration under the following conditions: Temperature, 80° C.; density of liquor, 60° Brix; filter aid, 0.385 per cent on weight of sugar solids; length of cycle, 30 minutes; pressure, 10 to 40 pounds at end of cycle. The above results were obtained earlier in the development of the apparatus, and while of satisfactory accuracy are subject to the objection that the intensities of the Tyndall beams are somewhat low for the close comparisons.

Table VII gives the results of another series of tests made with an entirely different raw sugar but with the same filter aids. In this case the apparatus used was exactly as shown in Figure 1. Clarity cuts in this case were taken at more frequent intervals of the last 15 minutes of the 30-minute cycle. The tyndallmetric results are expressed here first as foot-candles intensity and then as the reciprocals of these values, which gives figures that may be used more readily in expressing the clarities.

Table VII. Filtration of San Agustin Raw Sugar

Filter Aid	Time of Clarity Cut	Tyndall Beam Intensity	Clarity (Reciprocal of Tyndall Intensity)
	Min.	*Foot-candles*	
1	0–3	56.1	1.78
	3–6	25.0	4.00
	6–9	15.7	6.37
	9–12	11.5	8.70
	12–21	8.9	11.22
	21–30	8.0	12.50
2	0–3	43.3	2.31
	3–6	25.2	3.97
	6–9	15.7	6.37
	9–12	13.0	7.70
	12–21	10.6	9.43
	21–30	9.7	10.30
3	0–3	46.0	2.18
	3–6	35.0	2.86
	6–9	29.6	3.38
	9–12	25.2	3.97
	12–21	19.0	5.27
	21–30	15.5	6.45

Table VIII. Examination of Various Refinery Liquors

	Description of Sample	Tyndall Beam Intensity
		Foot-candles
1	60° Brix solution of refined sugar	6.5
2	First char liquor	9.4
3	First char liquor	10.2
4	Second char liquor	28.0
5	Thin char liquor	38.5
6	Dark colored char liquor, limed	38.5[a]
7	Very dark char liquor	44.0[a]

[a] Uncorrected for color

As illustrative of the utility of clarity measurements of refinery liquors other than filter-press filtrates, a series of tyndallmetric readings is given in Table VIII for various char liquors. These figures clearly show that readily

Table VI. Change in Degree of Clarification with Time of Filtration Cycle

Kind of Sugar Liquor	Filter Aid Used	Clarity of Filtrates Expressed as Intensity of Tyndall Beam 0–3 min.	3–6 min.	6–15 min.	15–30 min.	Particle Count per cc. × 10¹⁰ 15–30 Min. Fraction	Rate of Flow Gal./sq. ft./hr.	Liters/sq. meter/hr.
		Foot-candles						
Average filtering Hawaiian raw sugar	1	11.20	4.40	2.07	1.04	8.0	5.7	232.2
	2	5.80	3.15	2.08	1.78	21.6	16.9	688.5
	3	7.40	5.70	3.65	2.55	27.7	52.6	2143.0
Low filterability Cuban raw sugar	1	11.50	4.00	1.94	1.27	5.8	4.2	171.1
	2	5.05	2.76	1.76	1.28	21.6	10.0	407.4
	3	6.00	4.70	2.75	1.94	34.7	27.5	1120.4
Very easily refined Cuban raw sugar	1	3.65	2.18	1.16	0.93	14.3	8.6	350.4
	2	3.40	2.02	1.45	1.15	14.6	17.5	712.9
	3	5.00	3.60	2.45	1.64	30.0	44.6	1817.1

measured differences obtain in various refinery liquors. The liquors referred to here were obtained during regular operation at a typical Atlantic Coast refinery.

Further figures and comparative readings for these important refinery liquors under a variety of conditions cannot be given here. It may be stated, however, that the value of the apparatus for the examination of various refinery liquors, especially char liquors, is equally as great as for raw sugar filtrates. The same may be said for washed sirup.

Quality of Refined Sugars

The quality of refined sugars is reflected very strikingly in the clarity of concentrated sirups made up from the sugars. This test is recognized by refiners and by the trade as giving a valuable index of the purity of the sugars. Table IX shows the results obtained from the examination of a number of refined sugars.

Table IX. Quality of Refined Sugars as Shown by Tyndallmetric Readings

	Description of Samples	Intensity of Tyndall Beam
1	Highest quality refinery "specialty" sugar	1.0
2	High quality confectionery sugar	1.7
3	Highly purified sugar (laboratory process)	2.1
4	Refinery cube sugar	2.4
5	High quality beet sugar	2.7
6	Cuban refinery sugar No. 1	3.4
7	Granulated beet sugar	5.0
8	Granulated cane sugar No. 1	5.8
9	Granulated cane sugar No. 2	6.2
10	Granulated cane sugar No. 3	6.8
11	Cuban refinery sugar No. 2	7.4
12	Porto Rican vegetable char sugar	9.1
13	Granulated cane sugar No. 4	9.4

An example is given below of an actual refinery test to compare the effect of two different types of filtration upon the quality of the filtrates obtained. In this case the actual differences in the clarities of the filtrates was small and could not be determined with certainty by any means available at the refinery; yet the difference in quality of sugars eventually crystallized from these filtrates was recognized.

Table X shows the result secured by the Tyndallmetric examination of these filtrates.

Table X. Comparison of Paper Pulp and Diatomaceous Filter Aid Filtrations Conducted in Sugar Refinery

	Description of Sample	Intensity of Tyndall Beam: Filtrate from press	After concentration
		Foot-candles	*Foot-candles*
1	Liquor filtered with paper pulp	8.0	9.1
2	Liquor filtered with diatomaceous filter aid	7.1	8.3

The differences in the clarities of these two filtrates was confirmed in this case by extensive ultra-microscopic and colloid studies, the results of which agreed entirely with the tyndallmetric readings.

Other Applications of Apparatus

While beyond the scope of this paper, the authors wish to point out that the apparatus described has been tried for a number of turbidimetric and tyndallmetric measurements totally unrelated to filtration. The apparatus appears to be well suited for the accurate estimation of minute traces of chlorides, sulfates, etc., it being possible to determine amounts down to less than 0.01 part per million. Other applications, such as in biological work, are suggested.

Acknowledgment

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Corrosion in Sulfonators. Corrosion tests have been made at the plant of Endicott Johnson Corporation in coöperation with the International Nickel Company to establish the behavior of metals in sulfonators under actual operating conditions. The specimens insulated from one another were fastened on a spool-type specimen holder that was submerged within the sulfonator.

In the first series of tests the specimens were exposed during the sulfonation of 10 batches of neat's-foot oil by a process in which 66° Bé. sulfuric acid was added to the oil over a period of about 1 hour, after which the reaction proceeded for about 6 hours at a maximum temperature of 34° C. At the end of 6 hours a saturated sodium chloride brine was added to the mixture, which was then thoroughly agitated and allowed to settle overnight, after which the sulfonated oil was drawn off.

In the second series 66° Bé. sulfuric acid was allowed to react with cod liver oil over a period of about 6 hours, after which a 15 per cent sodium chloride brine was added and agitated as in the first case, allowed to settle overnight, and then drawn off. The oil was finally neutralized with alkali.

Corrosion rates were as follows:

Metal	Corrosion Rate. Mg. per sq. dm. per Batch: Sulfonated neat's-foot oil	Sulfonated castor oil
Lead	127	165
Chromium–nickel iron (18–8)	425	22
Nickel	30	25
Monel metal	34	11
Ni-Resist	90	29
Plain cast iron	10,000	120

Determination of *o*-Nitrotoluene in Nitrocellulose Powder by the Immersion Refractometer

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It became necessary recently in this laboratory to determine accurately the percentage of *o*-nitrotoluene in a straight nitrocellulose powder. The direct procedure of weighing the nitrotoluene, or determining its volume after extraction by ether, followed by removal of the ether by evaporation, is not possible because of the volatility of the nitrotoluene and the fact that some nitrocellulose is also dissolved during ether extraction of an ether-alcohol colloided powder. Determination of nitro compounds by the Dumas method is time-consuming. The use of the nitrometer for analysis of nitrotoluene (*3*) is not recommended, because of the difficulty in transferring the nitrotoluene without loss into the nitrometer. Callan and Henderson get accurate results with their modification (*1*) of the Knecht-Hibbert method (*2*). The Callan and Henderson method depends upon the reduction of the nitro group to an amino group by means of a titanous salt, followed by titration of excess reducing agent. The reduction is accomplished by boiling under a reflux condenser. Both reduction and titration are carried on in an atmosphere of carbon dioxide.

Whatever method is chosen the nitrotoluene must first be separated from the nitrocellulose. This process presents some difficulties, inasmuch as a small amount of nitrocellulose is inevitably carried along with the ether in an ether extraction. The authors used the immersion refractometer for determination of the nitrotoluene. This method is much simpler than the Callan-Henderson method, but can only be used after the nitrotoluene is obtained in a pure state.

The method, as finally developed, consists of extraction of the powder with ether, followed by heating the extract in a distillation flask on the water bath to remove all solvents, and then distilling the *o*-nitrotoluene by steam into a separatory funnel containing pure ether and a small amount of water. The ether, which now carries the *o*-nitrotoluene, is separated from the water, its volume accurately found, and the refractive index of the solution determined at 25° C. by an immersion refractometer. By comparison with a curve prepared from known standards, the amount of *o*-nitrotoluene is obtained directly.

Apparatus and Reagents

The Bausch and Lomb immersion refractometer was employed with a constant temperature bath at 25° C. Prism A was used. A 100-ml. distillation flask, with neck at least 15 cm. long and a side outlet near the top of the neck, was used in the purification of the *o*-nitrotoluene extract.

The ether used to dissolve the *o*-nitrotoluene was prepared from the ether manufactured in the Naval Powder Factory. After being redistilled, it was washed very thoroughly with water, then allowed to stand several days over calcium carbonate, and finally distilled over calcium chloride and sodium carbonate. It was stored in brown bottles, and kept in the refrigerator. Before being used to prepare the standard samples of *o*-nitrotoluene, the ether was shaken with water in a separatory funnel, so that it would be in the same condition as the ether in the actual analysis. Thus prepared, this ether gave a reading on the Bausch and Lomb immersion refractometer, using prism A, of 59.0 at 25° C.

Procedure

Extraction. Twenty grams of the sliced or crushed powder are extracted with pure ether for approximately 16 hours in a Wiley extractor. All of the *o*-nitrotoluene is removed from the powder grains by this treatment, the time required depending upon the fineness of the grains. The ether, when the extraction is finished, contains some alcohol and nitrocellulose, in addition to the *o*-nitrotoluene.

Treatment of Ether Extract. The ether extract is transferred to a 100-ml. distillation flask. This is closed with a stopper, carrying a thermometer, and is connected with another small flask filled with water to provide steam for distillation. The tube from this flask reaches nearly to the bottom of the distillation flask. The latter is heated on a water bath and the vapors of ether and alcohol allowed to go into the air through the side outlet until all the solvents are evaporated, as shown by the sudden rise of the temperature.

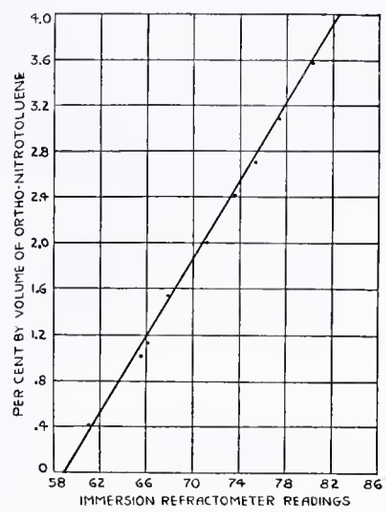

Figure 1. Readings on Immersion Refractometer *vs.* Per Cent by Volume of Ortho-Nitrotoluene of 1.168 Specific Gravity in Pure Ethyl Ether

No steam is used during this part of the distillation. The stopper of the distillation flask is loosened and the heating continued a minute or two to rid the flask of alcohol vapors. The entire process takes about one hour.

A water-cooled condenser is connected by means of a stopper to the side arm of the flask. The condenser is connected by means of an adapter to a 200-ml. separatory funnel containing approximately 30 ml. of pure ether, free from alcohol.

About 20 ml. of water are added to the distillation flask, the water bath removed, and the flask closed. The distillation is recommenced, using steam, but not otherwise heating the distillation flask, until all that remains in the flask, other than water, is a small amount of nitrocellulose.

The *o*-nitrotoluene, carried over by the steam, is caught in the separatory funnel and dissolved by the ether. When the distillation, which requires about one hour, is finished, the condenser and connections are washed with pure ether. The

ether is separated from the water and run into a 100-ml. glass-stoppered graduate. It is best to shake out the water in the separatory funnel with another portion of pure ether.

DETERMINATION OF *o*-NITROTOLUENE BY REFRACTOMETER. The ether containing the *o*-nitrotoluene is cooled to 25° C. in a constant temperature bath, and the volume noted. After determining and checking the refractive index, the percentage by volume of *o*-nitrotoluene in the ether solution is read from curve shown in Figure 1.

The volume of the ether solution of *o*-nitrotoluene, multiplied by the percentage by volume of *o*-nitrotoluene, multiplied by 1.168 (specific gravity of *o*-nitrotoluene), equals the weight of *o*-nitrotoluene in ether extract from powder.

PREPARATION OF CURVE. The curve shown in Figure 1 is made by testing known weights of *o*-nitrotoluene, specific gravity 1.168, dissolved in 25 ml. of pure ether, washed with water, with the immersion refractometer, prism A at 25° C. The volume of the *o*-nitrotoluene is calculated in milliliters from the weights and specific gravity and plotted on the curve against the refractometer readings as per cent by volume of ether solution. It would be more convenient for calculation to have a definite volume of ether solution, and have the graph give directly the weight of nitrotoluene in the sample. The authors found it simpler and perhaps more accurate, however, not to adjust the volume of the ether solution obtained at the end of the process. If the other method is preferred, the amount of ether solution can be set at a definite figure, say 50 ml., and the graph so adjusted that it will give directly the weight of nitrotoluene corresponding with any refractive index for this volume.

EFFECT OF ALCOHOL UPON REFRACTOMETER READINGS

Even as small an amount as 1 per cent of alcohol by volume in the ether changes the refractive index sufficiently to vitiate results. It is therefore necessary that all the alcohol be completely removed from the nitrotoluene.

ACCURACY OF METHOD

Standards were run as follows: 20 grams of nitrocellulose were placed in the Wiley extractor and extracted with ether for 16 hours. The ether was then transferred to a distillation flask and 2 ml. of alcohol and a known weight of *o*-nitrotoluene added. The process was then carried out exactly as has been described.

RESULTS SHOWING ACCURACY OF METHOD

Weight of *o*-Nitrotoluene Added	Weight of *o*-Nitrotoluene Found	Error
Grams	*Grams*	%
1.0286	1.0070	−2.1
0.8470	0.8344	−1.5
0.8800	0.8661	−1.6

TESTS ON ACTUAL POWDER

Determinations	Sample of Powder No. 1	No. 2	No. 3
Final volume of ether solution at 25° C.	44.0	46.0	45.5
Bausch and Lomb immersion refractometer reading at 25° C., prism A (scale divisions 0 to 100, prism A, cover a range of index values 1.3254 to 1.3664).	69.5	69.2	68.3
Per cent *o*-nitrotoluene corresponding to above refractometer readings	1.72	1.67	1.68
Volume *o*-nitrotoluene in cubic centimeters	0.7568	0.7682	0.7644
Weight *o*-nitrotoluene in grams	0.8839	0.8918	0.8928
Per cent *o*-nitrotoluene in powder not correcting for volatiles	4.42	4.46	4.46
Per cent *o*-nitrotoluene in powder correcting for volatiles and moisture	4.58	4.62	4.62

Twenty grams of powder were taken for each test. Total volatiles = 8.07 per cent.

The powder, when manufactured, was calculated to contain about 4.50 per cent *o*-nitrotoluene.

ACKNOWLEDGMENT

The authors wish to express their appreciation to Walter W. Farnum, chief chemist, Naval Powder Factory, for helpful suggestions, particularly that the refractometer be used for this method.

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Determination of Zirconium in Plain Carbon and Alloy Steels

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IN A PREVIOUS article (*1*) a method for the determination of zirconium, based on the rapid precipitation of $Zr(HPO_4)_2$ in the presence of varying amounts of a number of other elements, has been described. Inasmuch as several workers have experienced some difficulty with the procedure as outlined, and since complete precipitation of the zirconium in the presence of ferric chloride depends upon a rather close control of the acidity of the solution, the following details concerning the decomposition of the sample and the initial separation of zirconium are offered.

PROCEDURE

Five or 10 grams (depending upon the amount of zirconium present) of the drillings are transferred to a 600-cc. covered beaker and treated with hydrochloric acid (sp. gr. 1.19), 40 cc. being used for the 5-gram and 60 cc. for the 10-gram sample. The contents of the beaker is heated to 80° to 90° C. until all action appears to have ceased, when from 8 to 15 cc. of Perhydrol (30 per cent hydrogen peroxide) diluted with 25 cc. of water are introduced. The solution is heated for 1 or 2 minutes longer and diluted with warm water to 350 cc. Ammonium hydroxide (1 to 1) is added slowly until a permanent precipitate forms, followed by hydrochloric acid (1 to 1) dropwise, with stirring, until the precipitate just disappears. From 10 to 20 grams (a sufficient amount to reduce the iron to the ferrous state) of sodium sulfite dissolved in 50 cc. of hot water, and 20 cc. of hydrochloric acid (sp. gr. 1.19) are added in the order named and the contents of the beaker is stirred for 1 minute. Eight grams of diammonium phosphate dissolved in 50 cc. of water are added to the solution of 5 grams of steel or 10 grams to the 10-gram sample. The solution is stirred vigorously for several minutes and the determination completed as described (*1*). The final ZrP_2O_7 precipitate is tested for titanium as follows:

The ignited and weighed precipitate is fused with several grams (a sufficient amount) of sodium carbonate, the melt leached with

hot water, and the solution cooled to room temperature. The solution is filtered on a 9-cm. paper containing some ashless paper pulp and the paper and residue are washed 18 or 20 times with 2 per cent ammonium nitrate solution to remove sodium salts. The paper and precipitate are ignited in a platinum crucible at a dull red heat until the carbon of the filter paper has been completely burned, fused with 1 or 2 grams of potassium pyrosulfate, and the titanium is determined colorimetrically. The weight of titanium found, multiplied by 3.16, gives the weight of $Ti_2P_2O_9$ to be deducted from the combined weight of zirconium and titanium phosphates. The weight of ZrP_2O_7 found, multiplied by 34.39 and divided by the weight of sample taken, gives the percentage of zirconium. Should the amount of titanium found account for the greater part of the combined weight of zirconium and titanium phosphates, then it is suggested that more 30 per cent hydrogen peroxide be added than that used for the colorimetric determination and the zirconium precipitated by the addition of 3 grams of diammonium phosphate, digestion, filtration, and ignition as described in the previously cited article.

It is well known that $Zr(HPO_4)_2$ is completely precipitated from relatively strong hydrochloric acid solution in which the iron is present in the ferrous condition. Hence, in dealing with plain carbon and manganese steels the treatment with hydrogen peroxide may be omitted. However, in working alloy steels, especially those containing strong carbide-forming elements, the addition of hydrogen peroxide is necessary for the decomposition of the material.

The results obtained by the procedure described are shown in Table I.

Table I. Determination of Zirconium in Steel

Experiment	Kind of Steel	Steel Taken	Zirconium Added	Zirconium Found	Error
		Grams	*Gram*	*Gram*	*Gram*
1	Plain C	10	0.00047	0.00045	−0.00002
2	Plain C	10	0.00094	0.00093	−0.00001
3	Plain C	5	0.0045	0.00455	+0.00005
4	CrWV[a]	5	0.00235	0.00234	−0.00001
5	CrWV[a]	10[b]	0.00094	0.0009	−0.00004

[a] Bureau of Standards standard sample 50 A.
[b] Two 5-gram portions were taken and the precipitates combined after making the sodium carbonate fusion to separate the tungsten.

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Microburet for Potentiometric Microanalysis

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Results obtained by the junior author show that micropotentiometric titrations using 1 cc. or less of solutions with a normality of 0.1 to 0.01 are feasible and yield an accuracy in favorable cases of 0.1 to 0.2 per cent, provided the volume increments near the equivalence point are sufficiently small and uniform. The remarkable results just reported by Schwarz (*3*) more than confirm the authors' conclusions in regard to the applicability of potentiometric titration methods to small volumes. Their early results led to the development of a buret that delivers dependably single uniform drops with a volume of about 0.01 cc. Since graphical or, preferably, Hahn's methods (*1*) permit estimation of the end point to one-tenth of this increment, it is evident that the accuracy obtainable in suitable titrations is satisfactory for any ordinary micro uses.

Figure 1 shows the buret finally adopted. For convenience in cleaning and in building and adjusting the various parts, these were merely connected by high-grade clean rubber tubing at the places shown. A ground-glass joint could be substituted for the uppermost connection and the others could be eliminated by fusing the parts together, but this would involve considerable cost and inconvenience and would yield no increase in accuracy. The graduated section is obtained from a high-grade pipet graduated to 0.01 cc. and delivering 1 cc. The dimensions shown were found satisfactory and, in case of the tip, essential. The tip with the length shown has a capillary with an outer diameter of about 0.5 mm. It is paraffined by passing a continuous stream of low-pressure air through it while dipping momentarily into melted paraffin and then cooling till this solidifies. A tip that ceases to give small drops may often be repaired by connecting to the air supply and remelting the paraffin by holding it above a flame.

The braking capillary at the top is similar to that of Ormond (*2*) but made from ordinary glass tubing that is permitted to thicken in the flame and is then drawn out to a very fine capillary. The parts are then assembled as shown and with the stopcock open and the buret filled with water the braking capillary is shortened by breaking off small pieces until drops are delivered at the rate of 60 to 120 per minute.

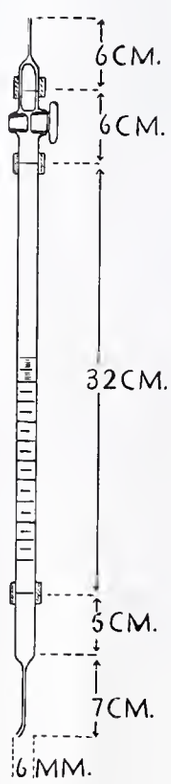

Figure 1

The next adjustment is that of the capacity of the tube above the stopcock. If this is too large, a single turn of the stopcock results in delivery of several drops; if it is too small, a turn does not always yield a drop. The capacity is adjusted by changing the length of glass rod inserted above the stopcock until single drops are obtained on turning the cock once.

In use the pipet is filled by removing the braking capillary and filling by suction through a piece of rubber tubing. In titrations the solution may be added rapidly until within 0.1 to 0.15 cc. of the end point. A few drops at a time are now added until the potential shows that the end point is approaching. The exact volume used thus far is now read with the aid of a lens and further additions are made in single drops until 3 or 4 drops past the end point. Since several minutes are usually required to obtain a stable potential, the exact volume may be read again in the immediate neighborhood of the end point. The exact end point is then determined by one of the methods mentioned and the volume read to 0.1 drop. The drop volume should be redetermined daily by counting the number of drops of the solution delivered between the 0.5- and 1.0-cc. marks. Since the drop volume depends partly on the hydrostatic head, very accurate work requires determination, once for all, gravimetrically of the relation between drop volume and buret reading, but this precaution is hardly necessary in ordinary work. The time required for a complete titration with this buret is not greater than that used with macroburets.

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Water of Crystallization in Total Solids of Water Analysis

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By including the water of crystallization in the sum of determined constituents, this sum becomes more strictly comparable to the total solids determined and provides a method of verifying the accuracy of the water analyses.

Calculation of Water of Crystallization

A MUCH better agreement is reached between total solids and the sum of determined constituents when the computed water of crystallization is included in the sum of determined constituents. The following definitions apply to these terms as here used:

Total Solids (solids in solution) is the mass of the residue obtained from an aliquot of water, after evaporation to dryness, heated to constant weight at a stated temperature, generally at 110° or 180° C. It is expressed in milligrams per liter of water (p. p. m.).

Sum of Determined Constituents is the total weight of ions and radicals present in water. It is likewise expressed in milligrams per liter of water (p. p. m.).

Water of Crystallization is the total weight of water retained by certain salts at a given temperature as an integral part of the molecule.

It has long been assumed that, as an aliquot of water is gradually evaporated to dryness, the ions present in solution form salts that pass into the solid phase in the reverse order of their solubility. The residue obtained at the end of the evaporation is a mixture of definite salts (exceptions are discussed separately), some of which contain water of crystallization.

Salts commonly found in waters may be arranged in the following order, beginning with least soluble and ending with the most soluble salt: calcium carbonate, magnesium carbonate, calcium sulfate, potassium sulfate, sodium chloride, sodium sulfate, potassium chloride, magnesium sulfate, magnesium chloride, sodium carbonate, potassium carbonate, calcium chloride, sodium nitrate, potassium nitrate, calcium nitrate, magnesium nitrate. This sequence is in the order of the weight of dissolved salt per 100 grams of saturated solution at 100° C. as shown by Seidell (*5*).

Silicates were not included in the list because of uncertainty as to the form in which silica occurs in waters having pH below 8.2 to 8.4 (the majority of natural waters) and of uncertainty regarding its solubility in hot solutions in the presence of other ions. Borates were omitted for the same reasons. In exceptional cases due consideration is given both to borates and silicates and these are treated separately.

In this laboratory all total solids determinations are made at 110° C. Other temperatures, as low as 103° C., would probably have been equally satisfactory and would not have resulted in any appreciable differences in the quantity of water held by the dried residue, although direct evidence in support of this view is not available. The "Official Methods" (*1*) recommend drying at 100° or 180° C. Individual investigators differ widely in their practices; Howard (*2*), for example, prefers drying at 180° C., and Zinzalian and Withrow (*6*) at 750° C.

Discussion of Changes during Evaporation

1. The first reaction brought about by the application of heat is the decomposition of calcium bicarbonate:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

The resulting calcium carbonate is only slightly soluble in hot solutions (0.40 milliequivalent per liter at 100°), and passes into the solid phase almost quantitatively in the early stages of the evaporation.

2. Magnesium carbonate is about twice as soluble as calcium carbonate. Its formation may be expected only when the concentration of HCO_3 exceeds that of Ca, and when Mg is also present. Normal magnesium carbonate, however, is, according to some investigators, immediately hydrolyzed to give magnesia alga, $3MgCO_3 \cdot Mg(OH)_2$. The exact nature of the precipitate formed upon evaporation of solutions containing Mg and HCO_3 ions is not known. Mellor (*3*) quotes Davis' summary of the divergent opinions of many workers in the following words: "All the varieties of basic magnesium carbonate, magnesia alba, light, heavy, and crystal magnesium carbonate are not definite salts but mixtures of the anhydrous and dihydrated magnesium hydroxycarbonates and hydroxide in varying proportions." The writer has somewhat arbitrarily chosen to represent the end product of the hydrolytic decomposition of magnesium carbonate as $3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. Seidell also uses this formula for basic magnesium carbonate. The loss of CO_2 in the hydrolytic decomposition of magnesium carbonate is here disregarded.

3. When the concentration of Ca exceeds that of HCO_3, and SO_4 is also present, calcium sulfate is next formed.

4. Sodium and potassium now join chloride to form sodium chloride and potassium chloride. Na and K are treated as a single factor, despite some differences in the solubility of their salts, because the concentration of K is, as a rule, very small in comparison with that of Na.

5. The remainder of Na and K, if any, combines with SO_4.

6. If both magnesium and sulfate are left after the precipitation of calcium sulfate, sodium chloride, potassium chloride, sodium sulfate, and potassium sulfate, they unite as magnesium sulfate.

7. If chloride exceeds Na and K and if some magnesium is still uncombined, magnesium chloride is also formed. Magnesium chloride, however, is not precipitated quantitatively as such, for it is subject to the following reactions: hydrolytic decomposition involving the loss of chloride as hydrochloric acid, formation of basic magnesium chlorides, double chlorides, etc.

Probably none of these reactions is quantitative and there is no satisfactory way of determining the relative proportions of the end products in any given case. The writer disregards them all in his computations, for indeed, in quantitative respects, the changes in weight of magnesium chloride due to these reactions would probably fall within the limits of analytical error.

8 to 12. The remaining anions and cations join each other and the resulting salts separate out in the reverse order of their solubility.

The following table summarizes the discussion:

Table I. Removal of Anions and Cations from Waters Undergoing Evaporation under Ordinary Atmospheric Pressure Based on Solubility of Salts in Grams per 100 Grams Saturated Solution

Order	Ions Combined	Formula at 110° C.	Reference
1	Ca to HCO_3	$CaCO_3$	Mellor, p. 812
2	HCO_3 to Mg[a]	$3MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	Mellor, p. 813
3	Ca to SO_4	$CaSO_4 \cdot 1/2H_2O$	Mellor, p. 535
4	Na and K to Cl	NaCl and KCl	Seidell, pp. 640 and 516
5	Na and K to SO_4	Na_2SO_4 and K_2SO_4	Seidell, pp. 667 and 556
6	SO_4 to Mg	$MgSO_4 \cdot H_2O$	Seidell, p. 396
7	Mg to Cl[a]	$MgCl_2 \cdot 6H_2O$	Seidell, p. 387
8	HCO_3 to Na and K	$Na_2CO_3 \cdot H_2O$[b] and $K_2CO_3 \cdot 2H_2O$	Seidell, pp. 633 and 508
9	Cl to Ca	$CaCl_2 \cdot 2H_2O$	Seidell, p. 196
10	Na and K to NO_3	$NaNO_3$ and KNO_3	Seidell, pp. 656 and 542
11	Ca to NO_3	$Ca(NO_3) \cdot 4H_2O$	Seidell, p. 207
12	Mg to NO_3[a]	$Mg(NO_3)_2 \cdot 6H_2O$	Hodgman-Lange, "Handbook of Chem. and Phys.," 12th ed., p. 219.

[a] An appreciable decomposition highly probable.
[b] At 105° C.

By following the principles outlined in the discussion and in Table I the water of crystallization held by the dried residue can be estimated, since the weight of the undetermined constituents and of the adsorbed water is generally small and falls within the limits of analytical error. By adding the computed water of crystallization to the sum of determined constituents, a theoretical weight of total solids is obtained.

It is a matter of routine practice at this Laboratory to make a comparison between the calculated and the determined total solids, whenever a "complete" analysis of a water sample is reported. A satisfactory agreement offers an assurance that the analytical work is free from major errors and that no constituent of importance has escaped attention.

On the other hand, knowing that in the determination of total solids losses of chloride and nitrate are practically unavoidable under certain conditions, as demonstrated by Howard (*2*), and that the presence of magnesium carbonate, abnormally high silica, or organic matter may become a source of an appreciable error, a 5 or 7 per cent difference between the calculated and the determined total solids may be looked upon indulgently, provided it can be traced to one of the sources previously enumerated.

Table II. Effect of Including Water of Crystallization in the Sum of Determined Constituents upon Agreement of This Sum with the Determined Total Solids

(Number of analyses, 280; range of total solids, 138 to 9714 p. p. m. From Water Samples Series 6070 to 7273, Rubidoux Laboratory.)

	Sum of Constituents Without H_2O of crystn.	Sum of Constituents With H_2O of crystn.
	%	%
Relative to determined total solids	94.9	99.6
Standard deviation	5.6	3.7
Average positive deviation from the mean	3.1	2.5
Average negative deviation from the mean	5.1	2.5
Number of items above the mean	175	138
Number of items below the mean	102	140

An illustration of the estimation of the water of crystallization held by dry residue at 110° C. is shown in the following analysis of water sample 6755, taken from the Colorado River at Yuma, Ariz.

Milliequivalents per liter: CO_3, trace; HCO_3, 3.20; Cl, 6.70; SO_4, 9.00; NO_3, 0.09; Ca, 6.25; Mg, 3.16; Na, 6.40; K, 0.16. SiO_2, 10.0 p. p. m.; total solids, determined, 1027 p. p. m.

By multiplying concentrations of the ions by the corresponding equivalent combining weights and adding the products, the sum of determined constituents was found—992 p. p. m. in this particular case (including SiO_2). Since it was known that one milliequivalent of bicarbonate in solution results in one milliequivalent of carbonate in the residue, the author used 30.0, the equivalent combining weight of CO_3 and 3.20, the concentration of HCO_3, to calculate the corresponding p. p. m. The water of crystallization was calculated in accordance with the principles outlined in Table I.

Table III. Water of Crystallization Held by Dry Salts

Step	Salt	Concentration	Corresponding H_2O of Crystn.
		Milliequivalents per liter	*P. p. m.*
1	$CaCO_3$	3.20	..
2	.....	..	..
3	$CaSO_4 . 1/2H_2O$	3.05	13.7
4[a]	NaCl and KCl	3.70	..
5[a]	Na_2SO_4 and K_2SO_4	2.86	..
6	$MgSO_4 . H_2O$	3.09	27.8
7	.....	..	..
8	.....	..	..
9	.....	..	..
10	.....	..	..
11	.....	..	..
12	$Mg(NO_3)_2 . 6H_2O$[b]	0.07	3.8

"Theoretical total solids" = 992 + 45 = 1037 p. p. m.

$\frac{1037}{1027} \times 100 = 101$, a satisfactory agreement.

[a] Na and K are treated as a single factor for the sake of brevity and on account of the low concentration of K.
[b] Probable partial decomposition of magnesium nitrate is disregarded.

Special Problem

Some natural waters are high in boron or in silica and highly alkaline. Calculation of the "theoretical total solids" in such cases constitutes a special problem. There were several waters of this type in a set of samples from Death Valley.

In order to calculate and correct the sum of constituents, the carbonate-bicarbonate titration value had to be reduced by the amount corresponding to the borate and silicate that were actually determined. In the case of soft waters such correction would often give low results.

Water sample 6074 (Amargosa Borax Works) upon analysis gave the following results: Milliequivalents per liter: OH, 6.70; CO_3, 21.60; Cl, 2.45; SO_4, 3.86; NO_3, 0.15; Ca, 0.11; Mg, 0.27; Na, 34.01; K, 0.84. B, 161 p. p. m. (corresponding to 577.3 p. p. m. B_4O_7); SiO_2, 93 p. p. m. (corresponding to 117.8 p. p. m. SiO_3); total solids, 2503 p. p. m.

Correction of the net titration value:

(161 p. p. m. B correspond to 7.44 milliequivalents B_4O_7; 93 p. p. m. SiO_2 correspond to 3.10 milliequivalents SiO_3)

True CO_3 = (21.60 + 6.70) − (7.44 + 3.10) = 7.76 milliequivalents

Calculation of the water of crystallization follows:

(*a*) $3MgCO_3 . Mg(OH)_2 \cdot 3H_2O$: 0.27 × 6.75 = 1.8 p. p. m.
(*b*) $K_2CO_3 . 2H_2O$: 0.84 × 18 = 15.1 p. p. m.
(*c*) $Na_2CO_3 . H_2O$: (17.76 − 0.27 − 0.84) × 9 = 150.0 p. p. m.

Note. $Na_2B_4O_7 . 10H_2O$ loses $5H_2O$ at 62°.

Adding the water of crystallization to the sum of determined constituents, the author obtained 2497 p. p. m. "theoretical total solids," which is 99.76 per cent of total solids as actually determined.

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Variable-Control Stillhead for Laboratory Columns

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THE apparatus herein described was developed largely from practical experience and research in analyzing the various synthetic solvent derivatives of pentane in the laboratory of the Sharples Solvents Corporation at Belle, W. Va. Data as to these products are found in Tables I and II of Clark (*3*).

In the manufacture of these pentane derivatives, a rigid alignment between control laboratory and the plant is essential. Rather stringent periodic checks and analyses were run on samples brought into the control laboratory during the various stages of the process. Since all stages of the process are interdependent, the analysis of samples was carried on frequently with a reasonable degree of accuracy. The bulk of these analyses involved Engler distillation runs, complex fractionations, simple volumetric titrations, specific gravity measurements, and other miscellaneous control tests. In the research department, a greater degree of accuracy was desired and the fractionation methods of the control laboratory were found to be inadequate for obtaining plant and sales specification data. One of the most desired specifications in solvent or lacquer formulation is obtained from the study of the boiling ranges. There are two possible methods: simple Engler distillation using no fractionation, and more complete fractional distillation using a high rate of reflux, repeating the fractionation until constant results are observed where an exact quantitative analysis is desired. By repeating fractionations several times, a good separation between substances of close boiling points—e. g., carbon tetrachloride, boiling point 76° C., and benzene, boiling point 80° C.—can be effected.

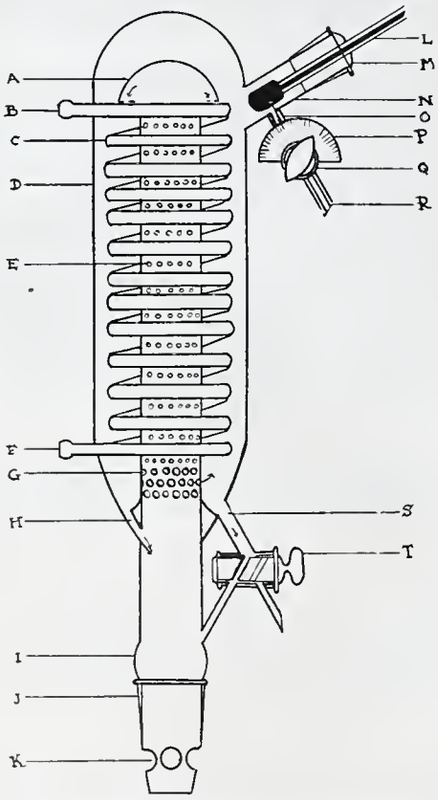

Figure 1. Diagram of Stillhead

In attempting to make exact quantitative separations, various types of columns were used and found to present manifold difficulties in design, control, and operation. The most obvious difficulty in using the ordinary columns was that of obtaining accurate thermometer readings at the vapor product take-off which would not be subject to changes resulting from the close proximity of the cold reflux as it returned from the side arm. As most commercial stillheads made no provision for the correction of this difficulty, the writer set out to design a stillhead that would not only remedy this condition but also would lend itself to variable control and further increase the efficiency of the column.

From the available literature of the past ten years (*1–35*), the writer found that, whereas an unusually large amount of excellent work had been accomplished in designing equipment for laboratory fractional distillation with especial emphasis on columns and their design, little attention has been given to designing adequate stillhead control equipment. Because there is a marked similarity in the essential requirements for stillheads and for laboratory columns, the writer drew freely upon this literature for theoretical and practical guidance. Many features of column design can be and some are incorporated in this design for an efficient stillhead.

The primary function of a fractionating column is to enrich the volatile components in the vapors arising from a still and to effect their separation by allowing them to interact with condensate originally produced by the partial condensation of the first vapors evolved. Efficiency is measured in terms of separating power of a definite unit of column length, while capacity is the measure of the quantity of vapor and liquid that can be passed countercurrently to each other in the column without priming or loading it. Efficiency is proportional to a factor expressing the time of contact between liquid and vapor. Differences in composition of the liquid phase in equilibrium determine whether a fractional separation of the mixture can be made. If there is no obvious difference, separation cannot be effected; if the difference is great, the separation is easy. The most effective method of obtaining a partial separation by fractional distillation is by passing the vapor through a countercurrent scrubber in which it is washed or scrubbed by liquid refluxed down the scrubber. The sharpness of separation under these conditions is dependent upon intimacy of contact of vapor and liquid in the column, thermal insulation of the column, and ratio of reflux to distillate. Too great a hold-up of reflux in the column materially decreases the sharpness of cuts. This difficulty can be remedied by making adequate provision for the free return of liquid and the free entrance of vapors into the column. The essential control of reflux usually depends wholly upon constancy of wall temperature obtained by controlling loss of heat through the walls. Efficiently controlled temperatures of the vapors leaving the top of the column are also of utmost importance in attempting fractionation where the regulation of the ratio of reflux to distillate is desired. A cooling agent functions here either to increase or decrease the refluxing action upon the vapors. The wide difference of opinion on the relative efficiencies of laboratory columns is believed to result from using such columns under different conditions of temperature, rate of distillation, etc.

The trend in column designing today is to produce all the refluxing or condensation at the top of the column in order to obtain the benefit of the total quantity of reflux through the entire length of the column.

Description of Apparatus

This design for a variable control stillhead embodies universally known principles which, however, have not been heretofore utilized in a similar manner. The underlying principle of this apparatus consists in providing for reflux by partial condensation of vapors and for complete and easy control of the reflux ratio. Partial condensation of the vapor has the same effect on its composition as has redistillation. The combination of both partial condensation and rectification with simple distillation, here used, affords an efficient means for separating volatile liquids.

The stillhead consists of the following essential parts: heavy-walled Pyrex jacket, dephlegmator tower, partial condenser, fluid control stopcock, controlled vapor take-off, and other miscellaneous accessories. The jacket *D* shown in the illustration is made of heavy-walled Pyrex tubing 5 cm. (2 inches) in diameter and 17.5 cm. high. It is rounded at the top advisedly to afford an ideal deflecting surface for the vapors. To cut down the radiation loss and diminish the draft effects in order to make this jacket as nearly adiabatic as possible, the exterior can be lagged with magnesia lagging or pipe covering, asbestos tape or twine, or the exterior can be covered with ordinary electrician's tape and coated with varnish afterwards. If a greater degree of accuracy is desired, the exterior can be silvered or, better yet, encased in an air-tight jacket. The dephlegmator tower *A* is made of ordinary 2-cm. Pyrex tubing about 24 cm. in height. To allow a free flow of vapor from the column the sides of this tower *A* are perforated with small orifices, *E*, about 1 mm. in diameter. These orifices are easily made by heating spots on the sides of the tower and puncturing these heated areas with a needle. The orifices below the condenser line, *G*, are intentionally made a little larger, 2 or 3 mm. in diameter, to permit the evolution of a greater amount of vapor for washing through the reflux collected in the lower part of the jacket *D*, which for all practical purposes serves as a secondary scrubber. Dephlegmator *A* is enlarged somewhat at *I*, providing for a fluid catch chamber to take care of the excessively large surges of reflux returning to the column.

The lower portion of the tower—that is, the part entering the fractionating column—is tapered somewhat to serve as a drip indicator and further perforated with larger vent holes, *K*, through which the vapor flows unhampered by the reflux returning to the column. This provision is made to eliminate the possibility of flooding the tower by the trapping of vapor. The joint assembly at *J* fits securely into the top of the ordinary laboratory fractionating column and can be fitted with any convenient standard interchangeable ground-glass connection. The gasket cushioned flanged ends devised by Othmer (*22*) may be substituted advantageously here. The joint as shown in the illustration is about a No. 15 size. For effective partial condensation of the vapor, a large area of condensing surface is provided for by the partial condenser *C* which has a condensing medium entrance at *F* and outlet at *B*. This condenser *C* is blown from ordinary soft glass tubing about 4 mm. in internal diameter. For liquids boiling below 70° C.—for example, amylene, isoamylene, or the pentanes—water is used as the condensing medium. A delicate regulation of the water supply can be obtained by using a needle valve or the ordinary laboratory screw clamp. For high-boiling liquids, kerosene or a regulated amount of air can be passed through the condenser instead of water. To indicate the temperature of vapor as product a glass-jacketed Fisher organic thermometer *L* fitted with a standard interchangeable ground-glass joint *M* is fixed in the thermometer well *N*. The vapor take-off *O* is made of ordinary heavy-walled glass tubing of about 2-mm. bore to avoid excessive hold-up at its junction with the thermometer well. *Q* represents a one-way ground-glass stopcock, preferably of the hollow type to allow for expansion changes at high temperatures. To the stationary member of stopcock *Q* is attached a calibrated protractor chart *P* over which moves a needle, attached to the male member by means of a V grooved inside the handle of the male member. With this arrangement, taken from Leslie and Geniesse (*14*), the cock can be opened accurately to any desired degree in the regulation of the vapor flow.

In order to minimize vapor leakage at the take-off *O*, it is advantageous to use a stopcock which cannot be dislodged easily under normal operating conditions. An excellent stopcock for this purpose is the one designed by Evans (*11*). He writes: "A hole is ground in the protruding end of the plug, in such a position that a small glass collar may be held firmly against the shell of the stopcock by means of a rather stiff piece of piano wire. The area of contact of the shell and small collar is ground and greased to permit ease of manipulation and the other face of the collar made concave to cause a small amount of tension in the wire."

The vapor take-off *R* can be connected to a product condenser of the Liebig type. To avoid loading of the stillhead by the accumulation of too much reflux at the lower portion or scrubber, adequate drain orifices are located at *H* and *S*. These orifices are pushed inward to drain off the excess liquid collected. The reflux take-off *S* leads to a standard three-way ground-glass stopcock *T*, which serves either as a regulator of the flow of reflux or as a sample take-off. With slight revisions of the apparatus, *T* can be arranged to charge reflux either back to the column or back to the original still as desired.

Conclusion

A rather crude working model of this apparatus without the later refinements was experimented with in the Sharples laboratory and was found to function very well in meeting the problem presented. The present design offers a number of experimental possibilities which the writer hopes to develop and elaborate upon later. With a few slight revisions, it may be utilized in the distillation of isomers, under reduced pressure. Aside from the control advantages which it offers, insuring uniform rate of distillation, it also possesses advantages in simplicity of design and construction, and absence of metals, corks, and rubber stoppers, thus eliminating corrosion or solvent problems. It also makes possible an even and uniform distribution of the reflux over the top of the column filling, which is conducive to the efficient operation of a relatively short fractionating column.

Acknowledgment

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Method for Determining the Dustiness of Coal and Coke

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Dustless coal and coke for domestic fuel have been a subject of intense interest in the sale of fuel. The rapid growth of interest and use of fuel treatment to allay dust led to the introduction of many materials for this purpose. The necessity of a quantitative method was soon recognized for the determination of the dustiness of solid fuels and also for comparison of the efficacy of the various materials suggested for treatment. A method and apparatus were consequently developed.

While the test is empirical and results obtained with treated fuels must be compared with blanks of the untreated fuel sampled at the same time, the usefulness has been proved through use over a period of years. Data obtained by this method are presented.

The treatment of solid fuels to allay dust at the time of delivery, and also to prevent dust after the fuel dries out in the householder's bin, was introduced several years ago. A rapid growth of interest by fuel merchant and producers ensued, resulting in a very general adoption of some form of fuel treatment. Calcium chloride was one of the materials suggested for the purpose, but a variety of other materials has also been proposed and offered to the trade. Spray manufacturers have also interested themselves in developing equipment for the small coal yard as well as for larger producers and distributors.

The principle of fuel treatment involves spraying with a solution or emulsion of some material which has the property of holding dust permanently to the individual pieces of fuel, or to agglomerate the dust so that it will not rise when the fuel is handled. Calcium chloride solutions are used because of the deliquescent properties of that salt. Other materials, such as oil, modified waste sulfite liquor, emulsions, etc., are also utilized. Any material used for fuel treatment must be both effective and cheap.

The problem of treating fuel resolves itself into selection of a material which will allay dust, selection of a satisfactory method of application, and determination of the quantity of material necessary to make the fuel substantially dustless.

It is evident that some method of quantitative determination of the dustiness of fuel both before and after treatment is necessary to make adequate comparisons of the effectiveness of various materials, quantities of treating agent, and methods of application. The Koppers Research Corporation has developed a method which has been in use since 1928, and, although it is empirical, it is believed that the results obtained are satisfactory.

Description of Apparatus

The method involves dropping a weighed quantity of fuel into a closed container and allowing the dust so raised to settle on a polished metal plate so that it can be removed and weighed. The apparatus consists of a box 1.52 meters high and 45.7 cm. square, arranged with a cover and having two horizontal slides inserted from the side. The top slide is 30.5 cm. below the top and, when inserted, makes a compartment in which the fuel to be tested is placed. The bottom slide is 61 cm. above the bottom and serves to collect the dust after the fuel has been dropped. Guides are placed so that the slides move easily. A drawer 30.5 cm. deep is located at the bottom of the apparatus, and provides a convenient means of removing the fuel after the test is completed. The entire apparatus is made of fairly heavy sheet metal and so constructed that it is dust-tight. The top slide is made of sheet steel and the bottom slide of rather thin sheet polished on one side—for example, stainless steel or chromium-plated brass. The inside surface of the apparatus is smooth from the top to the lower slide.

Method of Making Determinations

The top compartment of the box, made by the insertion of the upper slide, holds the sample of fuel to be tested. A sample of about 25 kg. is placed in this compartment and the cover closed tightly. It has been found more satisfactory to weigh the sample as taken rather than try to obtain exactly 25 kg. The lower (polished) slide, which has been brushed clean, is then placed in the guide extension in position for insertion. When all is in readiness for the test, the upper slide is withdrawn with one quick motion, thus allowing the fuel to drop into the drawer. Exactly 5 seconds later, as indicated by a stop watch, the lower slide is inserted and allowed to stand undisturbed for 2 minutes. At the end of that time the slide is removed and the dust which has settled on it is carefully brushed into a weighing bottle and weighed on an analytical balance. The weight of dust obtained is reported in grams per metric ton of fuel.

In addition to the above procedure, it has been found desirable in some cases to determine not only the dust which will settle in 2 minutes but also that which will settle in 10 minutes. This is accomplished by the use of two slides at the bottom. Both slides are inserted together 5 seconds after the fuel is dropped, and 2 minutes later the top one is withdrawn. The second slide is withdrawn 8 minutes later. The ratio of the two values gives a size-characteristic of the dust and is important in determining the efficacy of various treatments.

The dust tests should be made in a room free of strong drafts, so that no dust will be blown out of the sample or apparatus, and so that the settled dust can be transferred to the weighing bottle without loss.

Sampling

In sampling fuel for the dust test, extreme care must be taken so that the normal amount of dust will be retained.

It is obvious that the fuel can be tested as sampled with the

original moisture content or it can be tested after drying to remove moisture which would evaporate under storage conditions. In either case it is desirable to have a moisture determination at the time of the test. If the dustiness as sampled is to be determined, the test must be made immediately after sampling or else the sample should be stored in a moisture-proof container and tested as soon as practicable.

Figure 1. General View of Apparatus

However, if it is desired to determine the dustiness which may develop when fuel is stored under dry conditions, such as in a householder's basement, the sample is dried under controlled conditions as described below.

Drying Procedure

In order to determine the effectiveness of any dust-laying treatment for fuel, it is necessary to dry the sample under controlled storage conditions approximating very dry air conditions in the householder's basement. While an elaborate system of drying under controlled humidity conditions may be used, the following procedure is simple and gives satisfactory results:

Each 25-kg. sample is placed in a flat-bottomed container of not less than 61 cm. diameter. Large galvanized washtubs are satisfactory. The samples are exposed to the air for 10 days in a room whose temperature is maintained at 15° C. higher than the average outside temperature. The windows should be open but covered with muslin to keep out the dust and permit the higher temperature to be maintained in the room. It is desirable to obtain the relative humidity of the air in the room several times during the storage period and also at the time of the dust test.

When making comparisons of the effectiveness of various materials for dust-laying, samples of untreated fuel must also be included in each series of tests for comparison. It may be desirable also to include a sample treated with a standard amount of calcium chloride—e. g., 2 kg. per metric ton, in the case of coke.

The report of results on each dust test should include:

1. Description of fuel: source, size, point of sampling, etc.
2. Moisture content before spraying, when samples are obtained at point of treatment.
3. Material used to lay dust.
4. Weight of dust-laying agent and total volume of material or solution applied.
5. Length of time of storage.
6. Average temperature conditions during storage.
7. Average humidity conditions during storage.
8. Temperature and relative humidity at time of test.
9. Moisture content of fuel at time of test.
10. Amount of dust in grams per metric ton.

Agreement of Results

In Table I are shown the results of duplicate and triplicate determinations made on different solid fuels, with and without treatment with a dust-laying agent. The usual dust-settling period is 2 minutes, but a few determinations with a period of 10 minutes are shown for comparison.

Table I. Agreement of Tests

Untreated Fuel	Dust-Settling Period	Grams of Dust per Metric Ton		
		Test 1	Test 2	Test 3
	Min.			
Coke A	2	133	140	...
Coke B	2	131	157	...
Coke C	2	105	124	...
Coke D	2	140	131	138
	10	151	139	146
Coal A	2	134	106	130
Treated Fuel				
Coke A	2	33	28	31
Coke B	2	40	26	...
Coke C	2	40	32	...
Coke D	2	14.4	13.0	11.7
	10	14.6	13.1	11.9
Coal A	2	30	31	37

A rather interesting point is brought out by the results obtained from Coke D. The untreated coke shows an appreciable settling of dust beyond the 2-minute period. However, this same coke after treatment shows almost negligible dust beyond the 2-minute period, indicating that treatment has decreased the more objectionable fine dust to a much greater extent than the 2-minute figures indicate for the coarser and less objectionable dust.

Table II shows some data in regard to the effectiveness of various treating agents on coke, together with the amount required to give the result obtained.

Table II. Effectiveness of Various Treating Agents on Coke

Treating Agent	Quantity of Treating Agent	Dust in Treated Coke (Dried)
	Kg./metric ton	*Grams/metric ton*
A	0.70	10
A	0.45	20
A	0.35	29
B	0.90	42
C	1.75	21
D	1.20	80
E	1.45	50
Untreated coke (dried)	..	149

These samples were dried as described before testing.

This method has been used to determine the efficacy of treatment of various dust-laying agents, and upon that basis decisions have been made in the selection of the most satisfactory materials.

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A Study of Bunsen's Method

A New Apparatus

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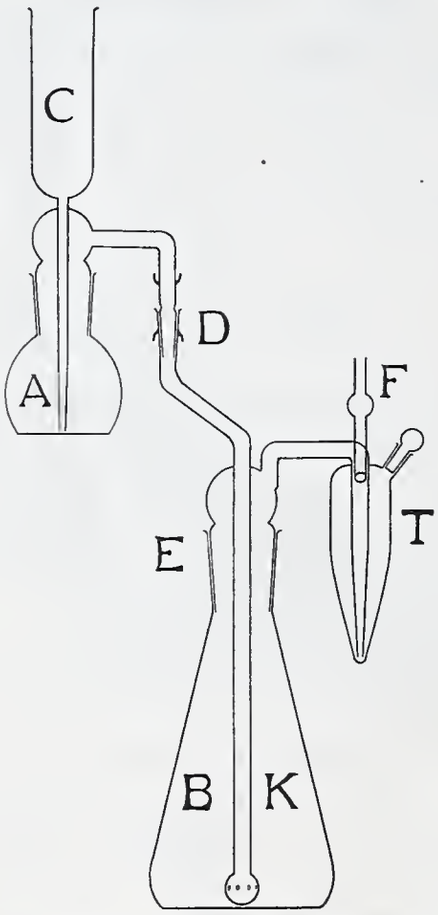
THE evolution method of Bunsen (*3*) has been the subject of numerous investigations for many years. These investigations have led to a better understanding of the mechanism of the method and a steady improvement of the apparatus.

Sherer and Rumpf (*17*) in their analyses of the oxides of manganese asserted the dependability of Bunsen's method. Fleck (*8*) applied this method to the analysis of lead dioxide with the apparatus which is described by Fresenius (*9*). Four years later Ebell (*5*) reported that excess concentrated hydrochloric acid and lead dioxide produced some chlorine,



Improved Bunsen Apparatus

but chiefly lead tetrachloride. His procedure was impractical. Topf (*18*) in his iodometric studies used the Bunsen apparatus so modified that carbon dioxide could be used to flush the system and prevent a suckback. His absorbers were Peligot tubes connected by rubber stoppers. Ullman (*20*) changed the apparatus so that the potassium iodide–iodine solution need not be transferred for titration. Marc (*14*) followed these experiments with an impractical apparatus.

Finkener (*7*) was one of the first to cast doubt on the efficiency of this evolution method. He stated that too little oxygen was obtained in the analysis of the higher oxides when hydrochloric acid was used to decompose the sample, but that good results were obtained when the sample was decomposed by dilute sulfuric acid and potassium iodide and by potassium bromide and hydrochloric acid. Farsoe (*6*) makes two departures in his experiments. First, he decomposed several oxidizing agents with 1 to 2 grams of potassium bromide, 20 cc. of concentrated sulfuric acid, and 80 cc. of water; second, he used an all-glass apparatus whose receiver had an inclined 10-bulb side arm as a trap. He claimed no reduction of the sulfuric acid, used carbon dioxide to flush the system, but did not state whether the titration was made in the receiver. Beck (*1*) in his experiments on red lead titrated the liberated iodine with standard arsenite solution in the presence of sodium bicarbonate.

Rupp (*16*), in general agreement with Finkener, stated that the chlorine which passed over during the distillation was reduced to a slight extent to hydrogen chloride and that the use of hydrochloric acid was worse than hydrobromic acid. He used the apparatus of Jannasch (*11*). Jander and Beste (*10*) supported Rupp's views and stated that the interaction of steam and chlorine can be overcome by using a delivery tube less than 40 cm. long and a decomposition flask of 50 cc. capacity. Wagner (*21*) used an apparatus somewhat similar to that described in this paper in his investigation of potassium chlorate and found no evidence to support Rupp's views with either hydrochloric acid or hydrobromic acid. The apparatus described here was devised and used by Buckwalter and Wagner (*2*) in certain bromination experiments. It was at the suggestion of Wagner that the authors applied this apparatus to Bunsen's method in the examination of the compounds which are reported. Le Blanc and Ebsrius (*12*), with an apparatus very similar to that of Farsoe (*loc. cit.*), report results on the oxides of lead in terms of oxygen.

All the chemicals which were used in these experiments were Baker's c. p. Analyzed.

Potassium Iodate was dried at 105° C. and the amount required for a 0.1 *N* solution was weighed and dissolved with gentle shaking in cold water. The solution was made up to volume.

Potassium Iodide, special crystals, iodate free, were dissolved in well-boiled water. The solution was prepared in small stock quantities and kept in the dark.

Sodium Oxalate was dried at 105° C. A stock solution was not used.

Hydrobromic Acid was allowed to stand over red phosphorus for 24 hours. It was filtered through asbestos into the flask of an all-glass still and distilled. The constant boiling fraction was collected in dark glass bottles and stored in the dark.

Arsenic Trioxide. The resublimed material was dried at 105° C. and the amount required weighed for a 0.1 *N* solution. It was dissolved in dilute sulfuric acid according to the method of Roark and McDonnell (*15*) and of Chapin (*4*).

Sodium Thiosulfate Solution was prepared by dissolving the salt in well-boiled water. The solution, approximately 0.095 *N*, was protected from light and carbon dioxide and frequently standardized.

Iodine was sublimed from potassium iodide and resublimed.

Potassium Permanganate. The pure crystals were dissolved in well-boiled water. The solution was allowed to stand, filtered through asbestos, and preserved in the dark in dark bottles.

Carbon Dioxide was generated from hydrochloric acid and pure calcite which had been placed in boiling water.

Starch. An 0.5 per cent solution of soluble starch was used. The solution was freshly made every few days.

Blanks were continually run on the chemicals and the apparatus and in all cases they were found to be zero.

The solid samples were weighed in one-gram weighing tubes.

By placing the tube well on the inside of the neck of flask *A* (cf. sketch) in a horizontal position and slowly tilting it to the vertical position, the greater part of the sample dropped from the tube. The tube was then dropped into flask *A*. Such a procedure prevented loss in transfer of the sample.

The apparatus was all glass with well-ground joints on which no lubricant was used. By moistening the joint with water and giving it a slight twist a perfect seal can be made. The volume of the decomposition flask, *A*, was 65 to 75 ml.; the receiver, *B*, 500 ml.; the trap, *T*, 25 ml. The tube, *C*, extended to within 2 mm. of the bottom of *A*, and tube *K*, to within 3 mm. of the bottom of *B*. It is advisable to place the receiver, *B*, in a beaker partly filled with cold water and to place a piece of asbestos between the beaker and the burner which is under *A*.

In the potassium iodide–sodium thiosulfate experiments the receiver contained 4.0 grams of potassium iodide in 160 ml. of water; the trap, 1.0 gram of potassium iodide in 20 ml. of water. In the arsenite-iodine experiments 35 to 40 ml. of standard arsenite solution were run into the receiver and diluted to 160 ml., and 5 to 6 ml. of the same solution, diluted to 20 ml., were run into the trap. The total volume of the arsenite solution was very carefully noted. Since the arsenite solution was acid, an excess of sodium bicarbonate was added just before the analysis was started. The use of arsenious acid and iodine in Bunsen's method was used by Treadwell and Christie (*19*) and later recommended by Lunge (*13*) on the grounds of expense.

When the proper solutions had been placed in flasks *B* and *T*, and the sample had been introduced in *A*, the delivery tube of a carbon dioxide generator was attached to the funnel, *C*, and the apparatus was flushed with the gas. (This first flushing was optional.) The proper acid was added through *C*, and a slow steady stream of carbon dioxide was led through the system. The contents of *A* were gently boiled until one-third to one-half its volume had distilled over. The flame was removed and the apparatus allowed to cool somewhat and then disconnected at *D*. Repeated tests at the exit of the trap for escaping halogen were always negative. The inlet tube and the trap are in one piece and fit into the receiver at the ground joint, *E*. The joint is just opened and the carbon dioxide delivery tube is attached at *F* and the contents of the trap are washed into the receiver with neither loss nor contact with air. The flushing of the trap with distilled water is accomplished in the same way. The solution in the receiver is ready to titrate in an atmosphere of carbon dioxide.

Experiment 1

The efficiency of the apparatus and the general procedure are shown against two sets of standard solutions—potassium iodate and potassium permanganate, and arsenious acid and potassium permanganate. The potassium permanganate was standardized against sodium oxalate according to the familiar method of McBride. The sodium thiosulfate was standardized against potassium iodate. Into the decomposition flask was run from a carefully calibrated pipet (25 ml. capacity) the potassium permanganate, which was decomposed with 8 to 10 ml. of concentrated hydrochloric acid. The liberated iodine was titrated with the standard sodium thiosulfate and from these titrations the normality of the permanganate was calculated. This result agreed with the sodium oxalate standardization.

A similar experiment was conducted with standard arsenious acid and potassium permanganate. Both hydrochloric acid and hydrobromic acid were used and the excess arsenite solution was titrated with standard iodine solution. These results agreed with the sodium oxalate standardization.

Normality of Potassium Permanganate

	Sodium Oxalate	$KI-Na_2S_2O_3$	Sodium Oxalate	$As_2O_3-I_2$ 10 ml. HCl	$As_2O_3-I_2$ 5 ml. HBr 15 ml. H_2O
	0.09378	0.09380	0.09370	0.09370	0.09366
	0.09380	0.09373	0.09370	0.09365	0.09366
	0.09376	0.09381	0.09370	0.09362	0.09362
	.....	0.09384	.....	....	0.09362
Av.	0.09378	0.09379	0.09370	0.09366	0.09364

Experiment 2

In the decomposition of the oxides of lead, concentrated hydrochloric acid must be avoided. Lead tetrachloride ($PbCl_4$) is readily formed from chlorine and lead chloride ($PbCl_2$) in the presence of concentrated hydrochloric acid and this compound is hard to break up under the conditions of this experiment. Therefore the concentration of the acid must not be too high. Any strength acid under 7.5 *N* was perfectly safe.

	$KI-Na_2S_2O_3$[a]	$As_2O_3-I_2$[a]	$KI-Na_2S_2O_3$[b]
	Red lead (expressed as per cent PbO_2)		
	34.21	34.12	34.15
	34.18	34.21	34.26
	34.15	34.12	34.15
	34.29	34.12	34.16
	34.29	34.13	34.15
	34.25	34.12	34.25
	34.23	34.13	34.23
Av.	34.23	34.13	34.19
	Lead dioxide (expressed as per cent PbO_2)		
	88.90	88.85	88.88
	88.84	88.83	88.93
	88.84	88.79	89.02
	88.92	88.82	88.92
	88.88	88.88	89.05
	88.84	88.82	89.03
	...	88.80	88.88
Av.	88.87	88.83	88.96

[a] Decomposed by 20 to 25 ml. 6 *N* HCl.
[b] Decomposed by 5 ml. HBr (sp. gr. 148) + 15 ml. H_2O.

Experiment 3

The analysis of the mineral pyrolusite presented nothing unusual. The sample which was taken for analysis was brought to constant weight by drying the sample in the weighing tubes at 105° C.

	$KI-Na_2S_2O_3$[a]	$KI-Na_2S_2O_3$[b]
	Pyrolusite (expressed as per cent MnO_2)	
	86.69	86.57
	86.50	86.61
	86.65	86.64
	86.74	86.60
	86.74	86.56
	86.70	86.74
	...	86.78
Av.	86.67	86.62

[a] Decomposed by 15 ml. 6 *N* HCl.
[b] Decomposed by 5 ml. HBr (sp. gr. 1.48) 15 ml. H_2O.

Conclusions

The Bunsen method applied to the decomposition and analysis of potassium permanganate, red lead, lead dioxide, and pyrolusite, is dependable and accurate.

Hydrobromic acid and hydrochloric acid are of equal value for the decomposition of the substances reported.

The arsenious acid and the sodium thiosulfate methods of estimation are both dependable, but the latter is to be preferred because only one standard solution is required, as against two in the former.

The apparatus which is described is easy to handle, requires a minimum of the operator's time, and can be adapted to numerous evolution methods. It is also excellent in students' hands.

Acknowledgment

The authors wish to express to E. C. Wagner of this laboratory their sincere thanks and appreciation for his numer-

ous suggestions during the course of this investigation on the apparatus which he designed.

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Automatic Pressure Regulators for Vacuum Distillation

II. Sulfuric Acid as a Manostat Fluid

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IN A PREVIOUS communication (*2*) a simple portable apparatus was described for the automatic control of reduced pressure during the vacuum distillation of organic compounds. In connection with further more exacting work, however, it was desired to increase the precision of regulation. In order to do this the authors have designed a second simple control (Figures 1 and 2) in which the final pressure adjustment is effected by means of a thermionically controlled flutter valve, and in which concentrated sulfuric acid is substituted for mercury as the manostat liquid. This combination is approximately ten times as sensitive as the previous unit and permits a regulation of ±0.015 mm. mercury at any pressure up to atmospheric.

THE THERMIONIC RELAY

The manostat contacts actuate the grid circuit of a 71-A type vacuum tube, which controls the operation of a 2000-ohm magnetic relay. The circuit is similar to that described in the previous paper, but operates in the opposite sequence—that is, closing of the grid circuit causes the plate current to flow and this in turn closes the relay. The latter lifts a rubber pad from a capillary inlet allowing air to leak into the system and establish the correct pressure. Needle valves of the conventional design (Hoke No. 304) are employed for rough adjustment of the air inlets, leaving the final flutter control to be effected by the relay system.

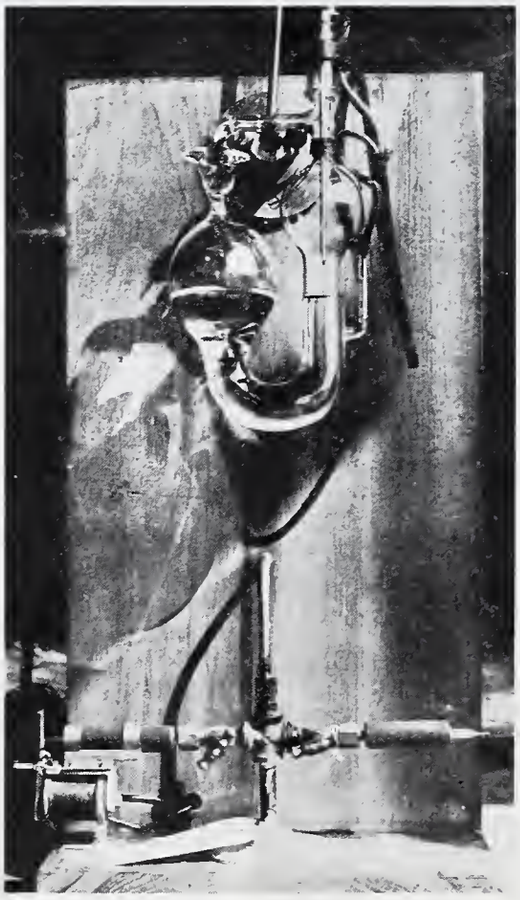

FIGURE 1. FRONT VIEW OF MANOSTAT

THE MANOSTAT

The manostat shown in Figures 1 and 4 combines several desirable features. It operates throughout the entire range of pressure, uses a minimum of fluid, and presents but little frictional resistance. The bulbs *B* and *C* (Figure 4) provide for a sudden change of pressure. The diameter of *B* is such that most of the motion is confined to the right-hand arm *A* and by tilting alone a range of ±2.5 mm. mercury may be secured. The manostat is constructed of Pyrex chemical-resistant glass with sealed-in platinum contacts *F* and *G*. External connection is made through mercury pools *H* and the center electrode is joined to a standard taper ground-glass joint *I* to facilitate cleaning and filling the manostat. The stopcock *J* is lubricated with vaseline only, rubber lubricants being more or less attacked by the acid. The manostat is sealed into the ground-steel joint with Picein or de Khotinsky cement.

Flexible rubber connections are avoided and manostat setting is facilitated by pivoting on the ground steel joint *K*, which serves as an axis for rotation. The joint is of stainless steel (Allegheny metal) both parts being cut at the same lathe setting with about a 14° taper and lightly ground together with 600-mesh silicon carbide. Vaseline is used as lubricant and the pressure of the atmosphere or check nuts suffices to

prevent turning when once the manostat is set at a particular pressure.

The Manostat Fluid

Because of its peculiar properties mercury has hitherto been universally employed as a manostat fluid. Its negligible vapor pressure, low viscosity, and high electrical conductivity make it particularly valuable in this connection, but these are to a large degree offset by its high density, enormous surface tension, and failure to wet the glass walls of the manostat.

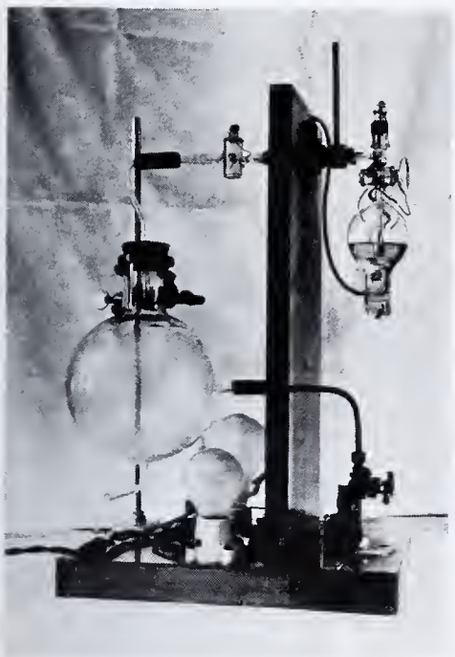

Figure 2. Side View of Manostat

It is readily attacked by common agents and the products of this chemical attack are usually insoluble in the bulk of the fluid, precipitating at the interface and forming a continuous film which must be broken before motion can occur.

Mercury adsorbs most substances powerfully but it is especially active towards its own compounds and it may refuse to recede from a plug of mercuric oxide or sulfide until a tension of some centimeters has been created. This describes an exaggerated case, but the factors are operative to a lesser extent even in very wide tubes. The conditions are at their worst after a slow motion in a tube which is free from vibration (*1*).

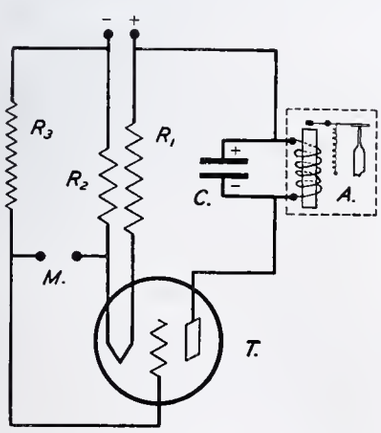

Figure 3. Universal 115-Volt A. C.-D. C. Thermionic Relay

A. 2000-ohm magnetic relay
C. 4-mfd. condenser, either foil or dry electrolytic type. If the latter is used the proper polarity must be observed.
M. Manostat contacts
R_1. 25-watt, 115-volt tungsten filament Mazda lamp
R_2. 40- to 50-watt, 115-volt tungsten filament Mazda lamp
R_3. 3- to 5-megohm resistor, 2-watt capacity
T. 71-A type vacuum tube

Considered as a manometer fluid it is true that some of these objections may be eliminated by providing a lubricant, but with manostats where the mercury must also play the part of an electrical switch, such a lubricant acts as an insulator which must be broken down or squeezed out from between the contacts before electrical connection can be established. On the whole, it is simpler to abandon mercury as a manostat fluid and to seek some other liquid which will combine high electrical conductivity, low density, low vapor pressure, and reasonable viscosity, with the property of wetting the manostat walls.

Sulfuric acid possesses approximately the desired properties. It wets the glass manostat walls, its density is about one-seventh that of mercury, and its conductivity is sufficient to permit use of a sensitive thermionic relay. It is, however, nearly fifteen times as viscous as mercury, and in order to obtain a comparable sensitivity under a given pressure head the manostat must be about four times the diameter of that for mercury, considering the latter as a perfect fluid and neglecting film friction.

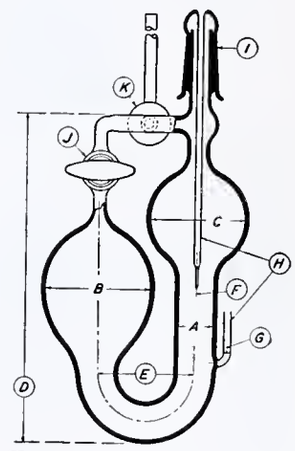

Figure 4. Sulfuric Acid Manostat

A. 2 cm. inside diameter
B. 6 cm. inside diameter
C. 2.5 cm. diameter
D. 17.5 cm.
E. 5 cm. on centers
F. 0.001-inch (0.025-mm.) diameter platinum contact wire
G. 0.005-inch (0.125-mm.) diameter platinum contact wire
H. Tubes filled with mercury to establish contact between the fine platinum wires and the external circuit
I. No. 11 I. S. T. ground-glass joint
J. 3-mm. bore stopcock
K. Ground-steel joint

Sulfuric acid (sp. gr. 1.84) when kept in vacuum evolves gases which tend to impair the setting of the manostat. It was found, however, that by using acid of sp. gr. 1.71 gas evolution was reduced to a negligible minimum, provided the manostat had been given the proper preliminary treatment. This consists in evacuating the filled manostat to a pressure of about 0.1 mm., boiling gently for 5 minutes, and allowing it to cool under vacuum. The manostat should subsequently be kept under vacuum when not in use by closing the 4-mm. oblique bore stopcock at the rear of the ground-steel joint. Under these conditions the rate of increase of pressure in the system per hour is less than the sensitivity of the manostat.

The Reservoir and External Connections

A reservoir of about 2 liters capacity is ample to absorb surges and serves as a convenient point to fasten the tubes leading to the pump and apparatus. A low-temperature vapor trap similar to that previously described (*2*) may be used to protect the mechanical pump from condensable vapors. However, since there are no valves in the gas path, and since the regulator itself is constantly being swept out by the incoming air or inert gas, the trap may be dispensed with when using a water suction pump, corrosive gases discharging with the water stream.

Operation

In operation the right-hand needle valve is manipulated so that the pressure is reduced to within 1 or 2 mm. mercury of the desired point as indicated by a sensitive mercury or butyl phthalate gage, and the manostat stopcock is closed. As the pressure continues to fall the acid rises in the right-

hand manostat arm. As soon as it touches the platinum contact the relay valve opens, allowing air to leak in until the electrical connection is broken. The manostat is then tilted until the desired pressure is reached, and a final close adjustment of the needle valves is made to eliminate surging. With the pump operating continuously the flutter valve oscillates at a frequency of from approximately 60 to 400 vibrations per minute. During operation excessive temperature changes of the room are to be avoided, since these will ultimately alter the setting.

ACKNOWLEDGMENT

Grateful acknowledgment of assistance is made to A. A. Morton, D. E. Bennett, and E. A. Averill.

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A Continuous Air-Lift Extractor

Application to Quantitative Determination of Benzoic Acid

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HAVING to determine the solubility of benzoic acid in sulfuric acid solutions over a wide range of concentrations, the authors have experimented with continuous extractors with the hope of effecting a saving in time and labor over that involved in the ordinary separatory funnel method of extraction. The usual type of continuous extractor for liquids (*3*, *4*, *5*), which depends on refluxing of the solvent, was found to be unsatisfactory because of the co-distillation of benzoic acid. Therefore an extractor was devised in which continuous circulation of the solvent (carbon tetrachloride) through the solution to be extracted and through standard sodium hydroxide is caused by means of a current of air.

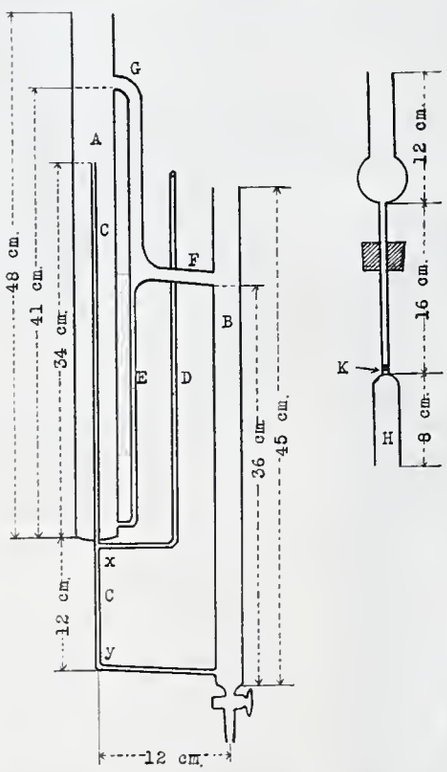

FIGURE 1. DIAGRAM OF EXTRACTOR

Inside diameter of *A*, 25 mm.; *B*, 16 mm.; *C*, *D*, and *E*, 5 mm.; *FG*, 10 mm.; cap *H*, 16 mm.

The extractor with the dimensions adopted is shown in Figure 1. In operation approximately 40 cc. of carbon tetrachloride are placed in *A* and 30 cc. in *B*. In all the subsequent discussion these amounts will be assumed. A weighed sample of the benzoic acid solution to be analyzed is superimposed on the carbon tetrachloride layer in *A* and water added until the tetrachloride rises in the side tube *E* to the level of the overflow tube *F*. An excess of standard sodium hydroxide is pipetted into *B* and this tube filled with water almost to the inlet. *B* is tightly stoppered and *A* stoppered with the cap *H*. A current of air entering through *D* raises a steady stream of drops of carbon tetrachloride through *G*. This tetrachloride trickles down through the acid solution, extracting benzoic acid, accumulates at the bottom of *A*, overflows through *F*, and trickles down through the sodium hydroxide solution, which in turn extracts the benzoic acid, and from the bottom of *B* is returned by the air current to *A*. Four hours' extraction was found by experiment to be satisfactory in the case of benzoic acid. At the end of this time the air is turned off, the liquid in *B* withdrawn through the stopcock, the tube rinsed down with water, and the excess sodium hydroxide titrated with standard hydrochloric acid in the presence of carbon tetrachloride which does not interfere in the titration. The separation of the carbon tetrachloride and aqueous layers in the apparatus is astonishingly complete. The air current is adjusted to give an even flow of solvent without undue splashing. Before entering the extractor, the air is passed through a tube of carbon tetrachloride to minimize evaporation of this substance in the extractor itself and through a 12-inch (30-cm.) U-tube filled with soda lime to remove carbon dioxide.

The extractor was constructed of thick-walled Pyrex tubing throughout. The large bore of tube *F* eliminates any possibility of siphoning. Since *G* opens into the acid side, the pressure in each side is always the same. The cap *H* prevents dangerous splashing if the air pressure in *D* accidentally becomes too strong, and the opening *K* in the tube attached to the cap forms an effective outlet for air and carbon tetrachloride vapor. The air inlet tube *D* is fastened to *F* by a short brace of glass rod (not shown).

The apparatus was found to be of sufficient rigidity and strength so that a bank of five withstood continuous use over a period of several months. Although these five were built by a professional glass-blower, the method was first tried out with a model which was constructed by an amateur glass-blower. Two spirals of glass rod (not shown) were inserted around the small tube *C* in order to break the tetrachloride into small drops and retard its rate of descent through the aqueous solution. The dimensions given are subject to considerable variation, but in changing them certain limitations should be kept in mind: The efficiency decreases with increase in cross section of *A* and *B*; *xy* must be of such length that the solvent will not be forced in the wrong direction by air pressure; and the relative heights of *C* and *F* must be decided with due regard to the relative densities of solution and solvent.

Of the solvents possessing the high density which this apparatus requires, chloroform and acetylene tetrachloride proved entirely unsatisfactory, probably because of hydrolysis of the solvent by the alkali (*1*, *2*). There was a large and continuing loss of titer of the alkali as extraction proceeded. To a much less pronounced extent the same difficulty appeared when carbon tetrachloride was used (*1*); in fact, it was pos-

sible to eliminate the resulting error by a small empirical correction.

In a large number of runs made with a known volume of standard sodium hydroxide in *B* and either water or sulfuric acid of concentrations up to 4 *M* in *A*, the loss in titer of the alkali varied from 0.05 to 0.2 cc. of 0.1 *N* solution. This loss was not due to carbon dioxide in the air, because the use of a much longer column of soda lime for its purification did not alter the effect; nor did it arise from the presence of acid impurities in the tetrachloride, which had been carefully treated to remove them. It cannot be due to splashing or to solution of sulfuric acid in carbon tetrachloride, since with 1 *M* sulfuric acid in *A* and water in *B* no titratable amount of acid was transferred to the water, and with 0.1 *M* sulfuric acid in *B* and sodium hydroxide in *A* no measurable decrease in acid titer was found. The loss of sodium hydroxide does seem to increase slightly with increasing concentration of sulfuric acid, but at any given concentration it is extremely regular.

To determine the correction, a standard solution of benzoic acid was prepared and aliquots of this solution taken for extraction from sulfuric acid solutions. From these data the volume of sodium hydroxide equivalent to the difference between the benzoic acid taken and that found was calculated and applied as the blank correction in the actual determinations. By interpolation, the corrections for other concentrations of sulfuric acid were obtained. Table I gives results typical of those obtained with benzoic acid and illustrates the precision which is possible. The same procedure was followed in making solubility measurements of phenylacetic acid.

The authors have found the extractor very valuable for the object in mind, and the apparatus or its principle may be useful to others who have determinations of organic acids or bases to make. It may be noted in the case of the latter that no loss in titer of the standard acid would result from the hydrolysis of the solvent, and that the correction necessary in the acid determination would disappear.

Table I. Extraction of Benzoic Acid from Aliquots of Standard Solution and Evaluation of Blank Correction

C_6H_5COOH Taken	Approximate Concentration H_2SO_4	C_6H_5COOH Found	Difference between C_6H_5COOH Found and Taken	Value of Difference in Terms of NaOH (0.1028 *M*)
Gram		*Gram*	*Gram*	*Cc.*
0.0287	3*M*	0.0301	0.0014	0.11
		0.0307	0.0020	0.16
		0.0305	0.0018	0.14
		0.0309	0.0022	0.17
		0.0310	0.0023	0.18
		0.0306	0.0019	0.15
		Av. 0.0306 ± 0.0002		Av. 0.15 ± 0.02
0.0708	0.75 *M*	0.0723	0.0015	0.11
		0.0718	0.0010	0.07
		0.0724	0.0016	0.12
		Av. 0.0722 ± 0.0002		Av. 0.10 ± 0.02

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Use of Glycerol in Iodometry

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The weighing of iodine for the purposes of standardization has always been attended by certain difficulties arising from the volatile nature of this element. In order to minimize the losses which occur, the iodine is usually dissolved in a solution of potassium iodide, the concentration of which may vary from 4 per cent to that of a saturated solution. Preliminary experiments indicated that the solution of potassium iodide itself lost weight. Popoff and Whitman (*3*) had previously found this to be true. Twenty milliliters of a saturated solution of potassium iodide, in an open beaker, were found to lose 6.4 mg. in 16 minutes and 63 mg. in 105 minutes, at 21.5° C. This loss, however, was greatly minimized when a glass-stoppered weighing bottle was used, and amounted to only 0.6 mg. in 49 minutes. With the stopper removed, the loss was 2.9 mg. in 22 minutes and 4.0 mg. in 93 minutes.

Effect of Addition of Glycerol

It seemed possible to develop a simple technic for weighing iodine in which it was not necessary to use glass-stoppered bottles. It appeared advantageous to be able to work in open vessels and to titrate the solution without having to transfer it. Preliminary experiments indicated that the presence of glycerol in the solution reduced the amount of iodine lost by volatilization. Consequently, known quantities of iodine were added to solutions containing glycerol and potassium iodide, as well as to solutions containing varying amounts of potassium iodide only. The open beakers containing the solutions were exposed to the air for about 13 hours, at the end of which time the iodine was determined by titration with a standard solution of sodium arsenite. It was found that the glycerol reduced the quantity of water lost and that there was no appreciable loss of iodine.

The following procedure was then used in standardizing a solution of sodium arsenite: Known quantities of iodine (approximately 1 gram) were dissolved in 20-ml. portions of a solution composed of 2 parts of glycerol and 1 part of a saturated solution of potassium iodide, contained in 250-ml. beakers. The weight of the iodine was determined by weighing the solution before and after adding the iodine. The normality obtained in one experiment, using chemically pure iodine of commerce, was 0.08242. The normality obtained in 8 experiments, using iodine from a different bottle of the same lot, ranged from 0.08225 to 0.08246 and averaged 0.08237. The normality obtained in 4 experiments, using specially purified iodine, ranged from 0.08233 to 0.08248 and averaged 0.08241. The titration was made electrometrically (*1*). In a previous study by the senior author, it was found that glycerol had no effect upon the electrometric end point. This is not the case, however, with the starch end point, which is affected by the presence of glycerol (*2*).

It appears, therefore, that the use of open vessels is permissible in the weighing of iodine for purposes of standardization, provided glycerol is present and the titration is made electrometrically. The chemically pure iodine of commerce, which is obtainable today, is of sufficient purity to be used without further refinement.

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Microbomb for Determination of Organic Halogens

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The determination of halogens in organic compounds by means of a sodium peroxide–sugar fusion in a microbomb using milligram samples has been accomplished. The results obtained over a wide range of compounds, only a few of which are published, indicate this method to be applicable to all organic halogens which may be determined in the standard macro sulfur bomb.

The determination of the halogen content of organic compounds by means of a sodium peroxide fusion in a macrobomb is perhaps the most rapid and efficient general method known. Parr in 1908 (*2*) discusses in a general way the applicability of the bomb fusion to the determination of arsenical and pyritical ores, copper, sulfur in rubber and silicon carbide, phosphorus, arsenic, sulfur, and halogens in organic compounds. The work by Lemp and Broderson, 1917 (*1*), as illustrated by their table of results, is somewhat incomplete. No attempt was reported to prove by experiment the explanations offered for discrepancies in many of the results obtained.

The bomb-fusion method for halogen determination has been in use under the author's supervision for two years and except in a few cases has given very satisfactory results.

Pure Nickel Bomb Cups

Bombs of various metals have been used, but the stainless-steel and the pure nickel bomb cups were found to be most suitable. Fusions from pure nickel cups have a decided advantage over those from stainless-steel cups. The solution of the fusion is water-white and the corrosion is much less in the nickel cups. The loss of weight as a result of 10 fusions in the stainless steel cup was 92.4 mg., whereas the loss of weight as a result of 10 fusions of the same substances in the nickel cup, conditions being about the same, was 6.7 mg.

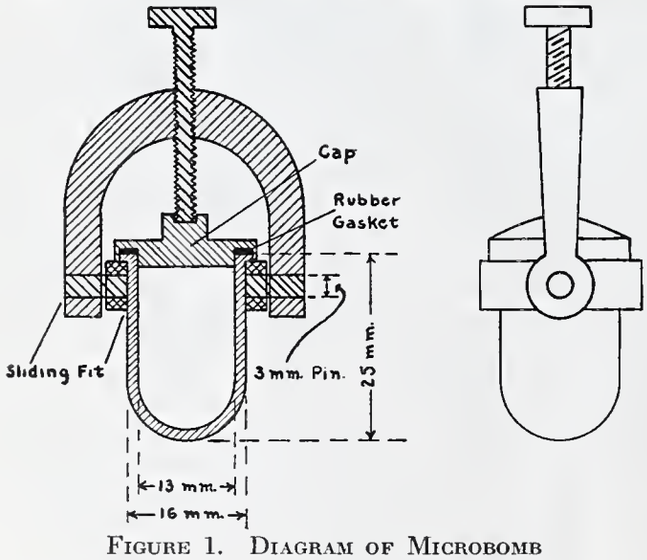

Figure 1. Diagram of Microbomb

Determinations Using Microsamples and a Microbomb

It was decided to investigate the possibility of using a small bomb for the determination of halogens in microsamples of materials. The bomb used in this work, illustrated in Figure 1, was made by the Burgess-Parr Company, Moline, Ill., of stainless steel. The apparatus used was the standard equipment for microgravimetric halogen determination with the bomb fusion replacing the distillation of halide in a hot tube by means of a current of oxygen (*3*).

The sample was placed in a bomb with 0.5 gram of sodium peroxide and 10 mg. of lactose. These were thoroughly mixed and the flame from a small burner was applied for 30 seconds. It was found necessary to wash the precipitate with 100 cc. of nitric acid solution (1 to 100) in order to remove all of the sodium nitrate.

The results obtained were not consistently correct and would seem to indicate that this method offers no advantage over the present micromethods.

Determination Using Semimicro Samples

It was then decided to determine the possibility of using the method for samples slightly larger than the strictly microsample.

The sample, which must be dry and finely divided, is so adjusted that the weight of silver halide obtained will be between 25 and 40 mg. One and one-half grams of sodium peroxide and 30 to 40 mg. of powdered lactose were used as the fusion mixture, and were well mixed by shaking thoroughly.

The cap with the gasket, which must not be pitted, is placed in position. The bomb is held in a small vise with lead-lined jaws and the clamp tightened with a wrench or pliers. A small flame is applied for 30 seconds and the bomb is allowed to cool for a few minutes in air and then dropped into a beaker of distilled water. The bomb is again placed in the vise and the clamp loosened. The cap is removed with a small pair of pliers and the under part washed into a test tube of 35 mm. inside diameter and 155 mm. inside length, preferably with a lip to simplify filtering. The test tube is of course provided with the usual microstand. The bomb proper is then placed in a suitable wire loop. It is advisable to use a noncorrosive wire, such as pure nickel. The outside of the bomb is washed off thoroughly with distilled water, lowered into the test tube, and placed on its side. The bomb is partially covered with water and the test tube covered with a watch glass. If the reaction does not begin immediately, it may be started by holding the test tube in hot water. After the reaction has ceased, the watch glass, the wire, and the wall of the test tube are washed down with water, hot in the case of chlorides and cold with bromides and iodides. The bomb is lifted by means of the wire and the whole carefully washed with water. The bomb proper must not be handled with the hands and when not in use should be kept in a closed container, which may be made from a small box fitted with a block of wood having holes of the same diameter as that of the outside of the bomb cup.

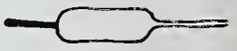

Figure 2. Tube

At this stage the liquid in the test tube should not occupy more than 15 to 20 cc. In the case of bromides and chlorides, concentrated nitric acid is added cautiously until the solution is slightly acid; 3 cc. should be sufficient. In the case of iodides a solution of nitric acid diluted 3 to 1 is added. The bubbles may be removed by stirring. The solution is now filtered into a second test tube, of the same dimensions as the first, through a 10-cc. Gooch crucible, which is fitted with a disk of good grade filter paper in place of the customary asbestos. This preliminary filtering is accomplished with suction and a convenient arrangement is to place the test tube in a large-mouthed bottle fitted with a two-hole rubber stopper. The Gooch is fitted into a tube, the farther end of which dips into the slanting test tube in order to avoid splashing. This filtering may be accomplished in 5 minutes. The sides of the test tube and the Gooch are washed

down, and finally the washings are tested to insure complete absence of halides. The tube containing the halide solution, the volume of which should be about 40 cc., is removed from the bottle and an excess of 0.1 *N* silver nitrate solution added. The precipitate is coagulated in all cases by vigorous stirring by means of a stirring rod, the end of which has been drawn to a dull point.

Preparation of Crucible and Treatment of Precipitate

The standard 10-cc. Gooch crucible was used throughout and found to be satisfactory. A smaller crucible if desired may be made by cutting off the top of the 10-cc. Gooch. Because of the small weight of the precipitate it was found advisable to prepare the Gooch in the following way:

Full suction is applied and a thick mass of suspended asbestos sufficient to form a layer about 3 mm. thick is added. The whole is macerated with a fine stream of distilled water and sucked dry, washed well with a hot chromic solution and hot concentrated nitric acid and then water, and tapped down with the blunt end of the stirring rod. The asbestos is then washed with 95 per cent alcohol, dried in an oven at 140° C. for 25 minutes, cooled on a copper block in a desiccator for 10 minutes, and allowed to stand in the balance for 15 minutes.

The precipitate of silver halide is filtered into the prepared Gooch by means of the pointed stirring rod. The test tube is washed finally with alcohol to insure complete removal of the silver halide and any adhering particles are removed with the feather. The precipitate is washed with 150 cc. of water, to insure complete removal of the nitrates, and then with a little alcohol, dried at 140° C., cooled and weighed as indicated above.

The precipitates may be weighed on a good macrobalance but the samples must of course be weighed on a microbalance.

Treatment of Liquids

The most satisfactory method of weighing liquids is by means of tubes prepared in the same way as the usual microtube (*4*). This method has also been used in the macroscale and gives good results. The semimicro glass tube should weigh not more than 20 mg. The macro tube should weigh not more than 90 mg. The tube found most suitable is illustrated in Figure 2. In all cases the tube should be centrifuged to remove the liquid from the capillary and then sealed. The tube is placed at the bottom of the microcup and covered with the peroxide-sugar mixture and the cap is locked in position. Good results were obtained without shaking the tube with the peroxide-sugar mixture or breaking off the capillary before placing the tube in the bomb cup.

Treatment of Iodides

Iodides require a slightly different procedure. Before acidifying with nitric acid, a few cubic centimeters of nearly saturated sulfur dioxide solution are added and, if upon addition of the nitric acid the violet color of free iodine appears, more sulfur dioxide solution is quickly added. The acid solution is filtered immediately and silver nitrate solution is added. The further treatment is that of the chlorides and the bromides.

Blanks on all reagents must be carefully determined.

This method was found to apply over a large range of organic compounds and Table I shows a few results obtained on some of the organic halogen compounds employed.

Table I. Halogen Content of Compounds Analyzed

Substance	Halogen Calculated %	Halogen Macro %	Halogen Semimicro %
p-Dichlorobenzene	48.25	48.16	48.19
		48.15	48.33
Dichlorophenol	43.52	43.41	43.55
		43.45	43.54
Bromocamphor	34.59	34.58	34.56
		34.53	34.56
Dichloraniline	43.78	43.77	43.73
		43.80	43.83
Dibromobenzene	67.76	67.70	67.59
		67.84	67.69
p-Iodoacetanilide	48.63	48.16	48.22
		48.12	48.08
Bromobenzene	50.91	50.78	50.78
		50.86	50.86
m-Dichlorobenzene	48.25	47.99	47.95
		48.11	48.06

The procedure followed with the macromethod is essentially that described above; standard macroapparatus is of course used, and the size of the samples so adjusted that the weight of silver halide will be between 225 and 275 mg. Larger samples have been used but are not to be preferred.

Summary

The halogen content of organic compounds may be determined by means of sodium peroxide–sugar fusion in a microbomb with about the same degree of accuracy and as rapidly as the macromethod. The weight of the sample required for analyses is much smaller than that required using the macromethod.

The method is applicable to all compounds which may be determined by means of the macromethod, and has the decided advantage that if the above directions are followed a destructive explosion is eliminated.

Compared to the microgravimetric method the determination of organic halogens is completed much more rapidly and is somewhat more accurate.

Acknowledgment

The author is indebted to F. Bremner and A. Kaellgren for checking results of analyses.

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(4) *Ibid.*, p. 70.

Received June 3, 1933.

Ground-Glass Junctions

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Those who have tried to make ground-glass junctions by grinding a tapered portion of a glass tube into a flanged end know that it is impossible to procure an evenly ground job. At any one time only a very narrow strip about the circumference is in contact. By using a hollow cone made of 0.03-inch (0.75-mm.) thick sheet copper one can grind each piece separately and then place the two together for a slight final grinding if necessary. The inside of the cone is used for the grinding of the taper and the outside for the grinding of the socket. The sheet copper is cut as shown in Figure 1, bent in the form of a cone, and soldered end to end. Standard dimensions call for an increase of 0.15 cm. in diameter for every 1 cm. measured along the axis of the cone.

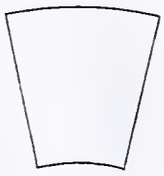

Figure 1. Sheet Copper

Figure 2

The cone can be mounted for the grinding by means of a one-holed rubber stopper and a 0.19-inch (5-mm.) wooden dowel placed in the chuck of the lathe or drill press. Turpentine or water is applied either to the copper or to the glass and powdered silicon carbide is added. This operation is repeated until the grinding is of the desired depth. Copper is used in such grinding operations because it is extremely tough, yet soft enough to let the fine particles of carborundum imbed in it and grind away the glass. By using a hollow cone of copper the same slope is assured for the taper as for the socket.

Received July 24, 1933.

New Machine for Laboratory Evaluation of Fatigue of Rubber Compounds Flexed under Compression

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THE failure of rubber compounds to resist fatigue when subjected to flexing under compression, or their tendency to "blow-out," has always been a serious problem, and is becoming an even greater limiting factor in all phases of rubber technology. A new machine has been developed recently in the laboratories of The Firestone Tire and Rubber Company for the measurement of fatigue resistance of rubber compounds.

Previous machines of this type have usually been large wheels or drums on which whole tires have been run to destruction. The laboratory machines have not been very numerous or very successful. The Schopper detrition tester (*2*) is a laboratory machine for testing the fatigue and abrasion resistance of rubber stocks in the shape of small balls. Abbott (*1*) obtained blow-outs in his laboratory work on testing rubber used to absorb vibration. Many suggestions have been advanced as to how correct laboratory evaluation of fatigue resistance might be accomplished. The design finally adopted (Figure 1) was made up by Raymond W. Allen, of the Firestone engineering staff, in whose name the patent application on this Flexometer has been made.

A photograph of the instrument is shown in Figure 2. The Flexometer is definitely a laboratory testing device, but is sufficiently rugged to withstand hard and continuous service. The operation of the machine simply consists of compressing, under definite load, a block of rubber between two plates, one of which is stationary and the other travels in a circular motion of definite magnitude. The plate oscillates 800 times per minute, this speed being constant under all conditions. Both the loading and the magnitude of the circular motion may be varied widely. The machine has almost unlimited possibilities in evaluating stocks, since the working conditions in any compression service may be simulated.

The laboratory test block used is in the shape of a frustum of a rectangular pyramid, of which the base is 2.125 × 1.125 inches (5.40 × 2.86 cm.); the top, 2 × 1 inches (5.08 × 2.54 cm.); and the altitude, 1.50 inches (3.81 cm.). This tapered shape was selected so that perfect blocks could be prepared from any type of stock. Those with high zinc oxide content, for example, are very brittle while hot. If the test blocks of such stocks have any tendency to adhere, they may be ruined in stripping from the mold. Test blocks of cured articles may be cut into any size and shape, provided their height is not more than 2 inches, as this is the maximum distance between plates. The tapered block is used only when the test sample must be cured in the laboratory.

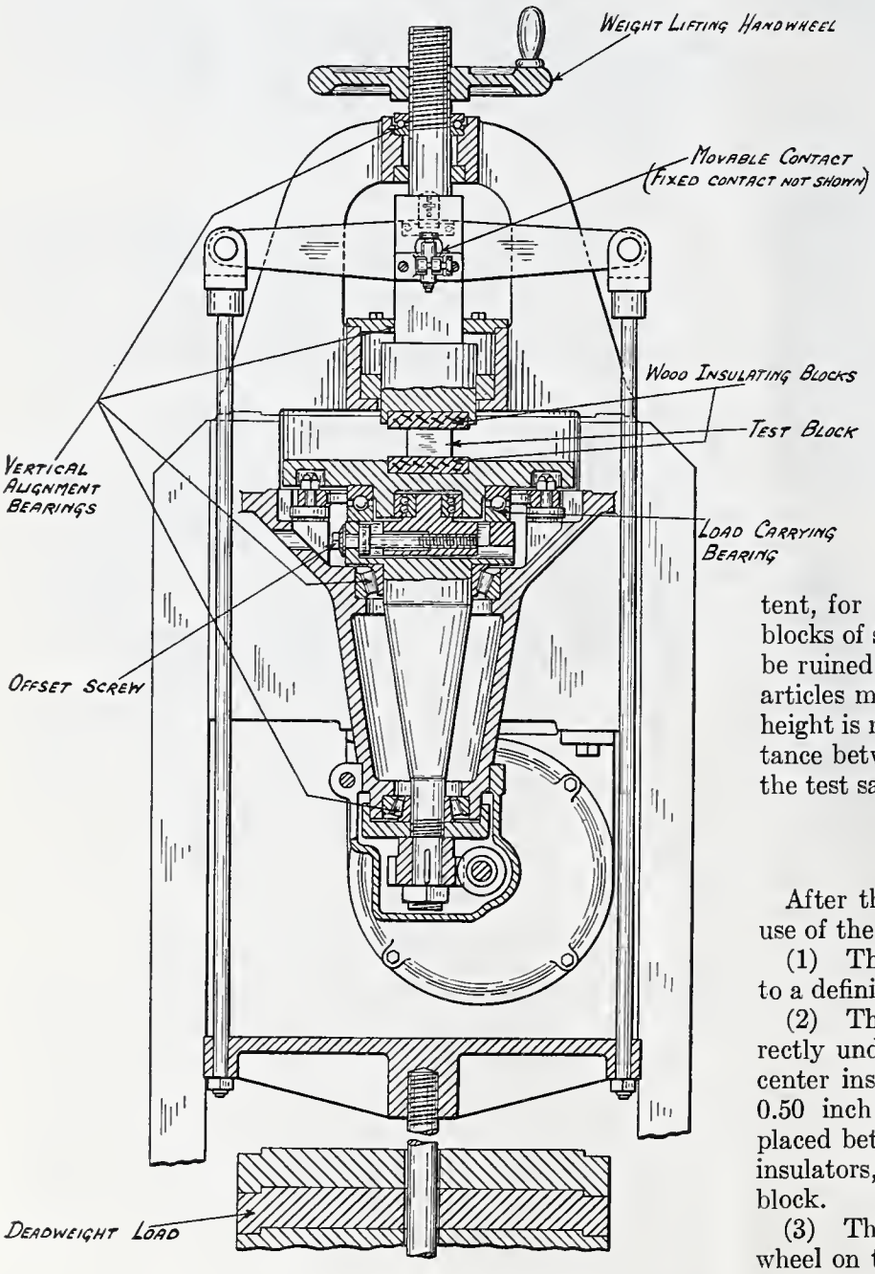

Figure 1. Diagram of Flexometer

Procedure

After the test blocks have been made, the procedure for use of the machine is as follows:

(1) The oscillating plate is set on dead center and brought to a definite starting temperature.

(2) The test block is placed on the oscillating plate, directly under the loading plate. Each of these plates has a center inset of wood, 3 inches (7.62 cm.) in diameter and 0.50 inch (1.27 cm.) thick, and the rubber test block is placed between the wooden blocks. The latter act as heat insulators, and tend to hold all generated heat in the test block.

(3) The load is applied to the block by turning the hand wheel on top until the load is carried by the block and not by the thrust bearing on the wheel.

(4) The height of the block after applying the load is then measured, and the deflection is calculated.

(5) The oscillating plate is set the desired amount off center, distorting the test block so that it resembles the frustum of a sloping rectangular pyramid. The diameter of the circle described by the lower plate while in motion is designated as the "throw."

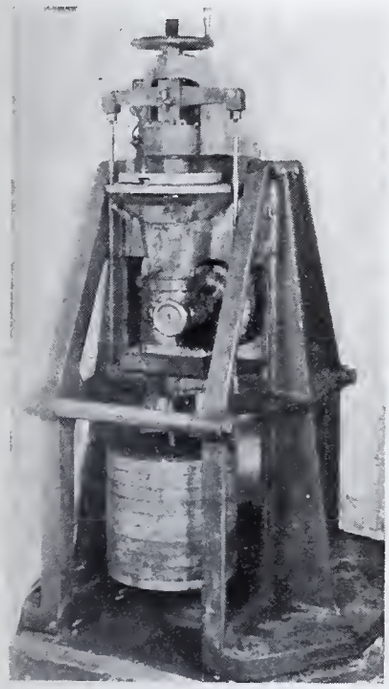

Figure 2. Photograph Showing Flexometer

(6) The electrical bell-ringing contacts are adjusted so that they are a definite distance apart. This initial contact opening is called "signal distance." As the block is deflected under the testing conditions, the upper contact is carried downward toward the lower contact, because the load, which is a dead weight, continues to rest on the yielding block. This downward movement has been found by many tests to be a definite criterion of the condition of the center of the block. In other words, all blocks of similar composition have yielded the same distance, or signal distance, at the time porosity began. Should the test be continued sufficiently long, the block will actually blow-out, or shatter to pieces, and it is to prevent this actual destruction that the yield distance of slight porosity is used.

(7) The duration of the test, which is now ready to be started, is measured from the time the circular motion is started until the bell rings. The bell does not ring until the test block has been deformed sufficiently to allow the electrical contacts to close.

Table I. Special Stocks Used in Tests

Stock	A	B	C	D	E	F
Smoked sheet	100	100	100	100	100	100
Sulfur	3	3	3	3	4.5	3
D. O. T. G.	1.5	1.5	1.5	1.5	1.5	1.5
Channel black	8	36	36	36	36	8
Pine tar	1	1	5	...	1	1
Mineral rubber	...	...	...	5	...	...
Zinc oxide No. 1	180	90	90	90	90	...
Zinc oxide No. 2	...	...	...	...	...	180

Cure, 60 and 80 minutes at 290° F. (143.3° C.) on regular taper blocks.
Testing conditions: load, 550 pounds (249.5 kg.); throw, 0.55 inch (14 mm.); signal, 0.300 inch (7.60 mm.)

Table II. Data Obtained with Flexometer

Stock	Hardness 3-Pound Penetrometer	Deflection	Time until Bell Rang	Condition of Stock after Test
	0.001 in.[a]	%	*Min.*	
60-minute cure				
A	43	23.3	53	Slightly porous
B	35	22.3	16.5	Porous
C	35	23.3	10.5	Porous
D	35	22.7	17.5	Porous
E	30	18.0	19.5	Porous split
F	40	22.7	31	Slightly porous
80-minute cure				
A	46	22.3	63	Slightly porous
B	35	22.3	16	Porous
C	33	23.0	10.5	Porous
D	35	22.7	17	Porous
E	29	17.3	20	Porous split
F	40	22.7	39	Slightly porous

[a] Equivalent to 0.00254 cm.

The operation evaluates resistance to blow-out. Temperature rise data or heat generation measurements may also be made by inserting thermocouples and taking temperature measurements after a certain amount of work has been done on the block.

One man can operate at least five of these machines efficiently, or if an automatic stop is installed, one machine can be operated without seriously interfering with other work the operator may be doing.

Care should be taken that only well-molded blocks are used and that the machine is correctly set each time. If these two precautions are taken, consistent results will be obtained. The machine is not intricate in design or movement, yet it can readily be used for a wide variety of tests.

Results

As an example of the results obtained on this machine, six special stocks were mixed and tested. Their formulas and the data obtained are given in Tables I and II.

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A Circulator for Ice Water

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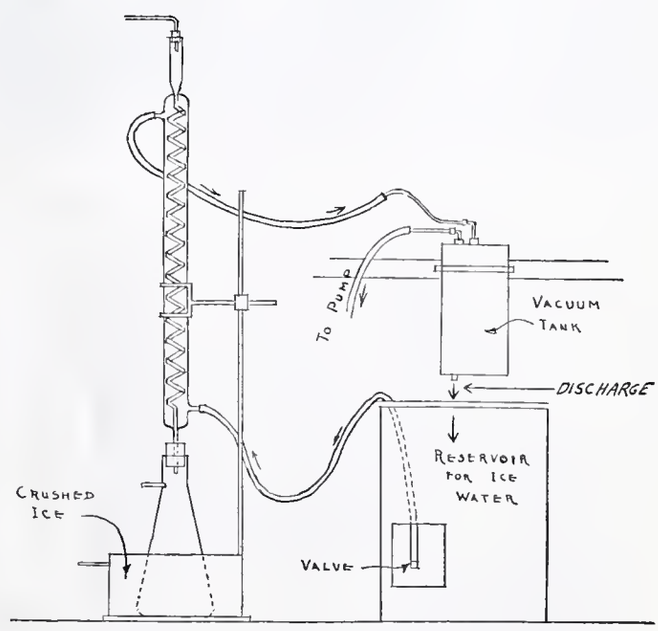
A SECOND-HAND automobile vacuum tank purchased at a wrecking establishment and operated with a small filter pump has been very satisfactory for circulating ice water through a condenser during the distillation of low-boiling liquids. The tank is mounted vertically on a laboratory shelf or wall so that it discharges into a suitable vessel containing a piece of ice and a small amount of water. The circulation is intermittent, and while the vacuum tank is



discharging some of the water in the condenser will run back into the reservoir, unless a valve is placed in the intake hose. A suitable valve may be obtained from an old atomizer bulb. With this outfit, 10 pounds (4.54 kg.) of ice will operate a condenser for 3 to 4 hours.

Received June 15, 1933.

A Mechanically Operated Buret

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It has recently (*1, 3, 4*) become feasible to record continuously electric potentials related to the pH or oxidation reduction potentials in a rather wide variety of mixtures. Such records greatly increase the usefulness and possibility of automatic controls. The mechanically operated buret here described was designed to add sodium hydroxide solution to a reaction mixture as required to maintain a constant e. m. f. The reaction might continue several days.

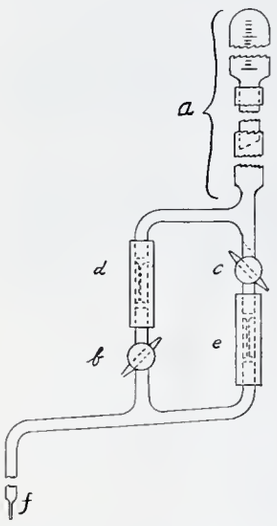

Figure 1. Mechanically Operated Buret

Description of Apparatus

The measuring and recording apparatus used with this buret is a Leeds and Northrup recording potentiometer, together with a calomel-antimony cell or a calomel-glass cell and a vacuum tube amplifier described by Stadie and co-workers (*2*). These cells were chosen because they neither require that portions of the materials be discarded, nor that foreign materials, such as hydrogen, quinhydrone, or color indicators, be added to the mixture. Changes in the e. m. f. of the glass cell are also unusually specific for changes in pH. The potentiometer controls a dropper through two contacts or switches (*L* and *H* of Figure 3). For the slow rate both the controlling contacts, *L* and *H*, of the recorder are closed. For the fast rate contact *H* is open and contact *L* is closed.

The dropper is a device for adding small and constant, but adjustable, amounts of alkali at regular intervals and additional amounts as needed, at slow or fast adjustable rates. The dropper consists of a special buret and a mechanism for opening its stopcocks. The main features of the dropper are: intermittent rather than continuous flow of the liquid; separation of the section of capillary tubing, which limits the rate of flow, from both the stopcock and the tip; and provision of an adjustable but fairly constant level from which the controlling liquid is supplied.

The buret is shown in Figure 1. It includes a reservoir (*a*) to supply the solution at an adjustable constant head; two stopcocks (*b* and *c*) to be opened at controlled and regular times, respectively; two capillary tubes inclosed in rubber connectors (*d* and *e*) to regulate the flow when the stopcocks are open; and the tip (*f*) which controls the size of the drops discharged. The internal diameter of the tip is larger than the capillaries to prevent clogging. Its outside diameter is sufficiently small to give about 50 drops per cc. After several runs, the reservoir (*a*) was replaced by a bulb hung from one arm of a balance and connected by a small flexible rubber tube to the stopcocks. An automatic weighing and recording device is being developed for this balance.

The mechanism for opening the stopcocks is shown in Figure 2. Two disks with crank pins (1 and 2) are mounted on ends of two parallel shafts (11 and 12). Two gears (9 and 10) are mounted on the opposite ends of these shafts, and the shafts are placed so that the gears are in the same plane and on opposite sides of a common drive shaft and worm (15 and 16). Two other disks (3 and 4) are mounted on shafts (13 and 14) parallel to the gear shafts. The shafts and bearings 11, 12, 13, 14, and 15 are bicycle hubs mounted in two frames (23 and 24) which were cut from $^3/_8$-inch iron plates. The plugs of the two stopcocks (*b* and *c*) are attached to disks 3 and 4 by the universal joints 7 and 8, respectively. Adjustable rocker arms (5 and 6) are also attached to the disks 3 and 4, respectively, and are rocked by pins in disks 1 and 2, respectively. Slots in the disks (3 and 4) and in the rocker arms allow adjustment to open the stopcocks by suitable amounts, and for suitable fractions of each revolution of disks 1 and 2. When alkali is not

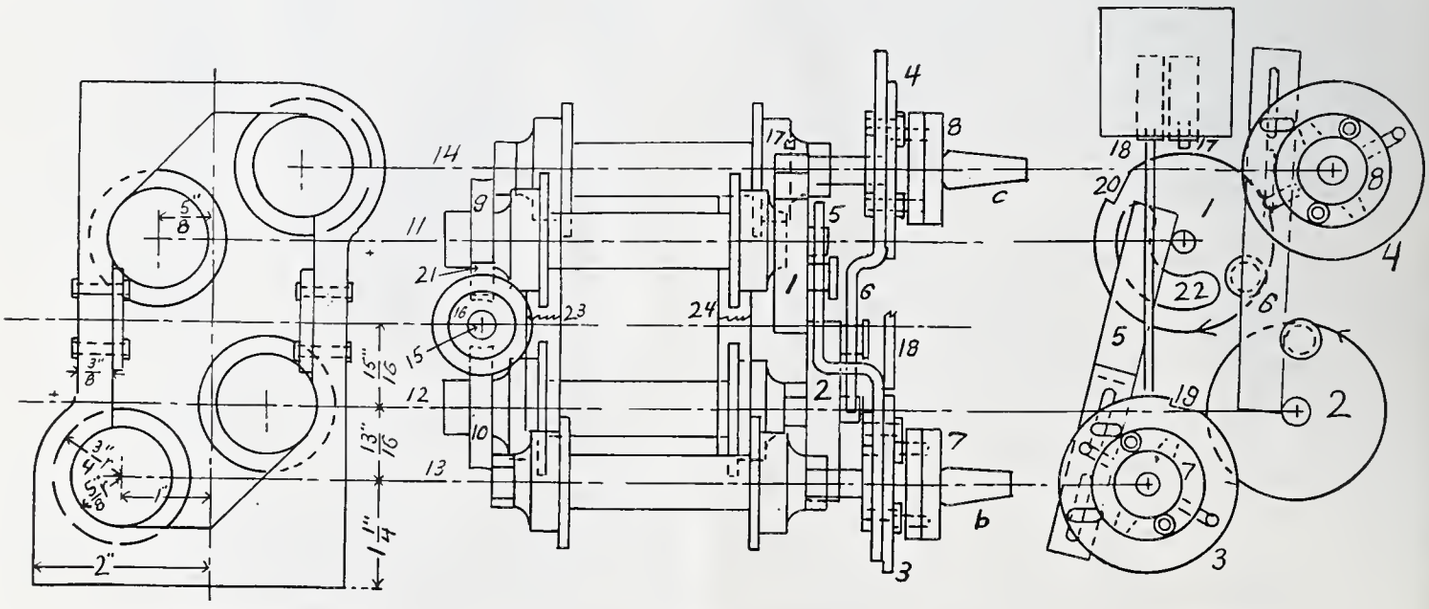

Figure 2. Mechanism of Opening Stopcocks

needed, the stopcocks are kept closed, and the free ends of the rocker arms are held against the shafts, 11 and 12, by rubber bands not shown. Enough teeth were removed from gear 9 to provide a position at which it will not mesh with the worm, 16. This sector (21) is so located with respect to disk 1 that the gear is free about 10 circular degrees before the pin comes in contact with the rocker, 5. A weight not shown, or the lack of balance caused by the hole (22) in disk 1, pulls the gear past the free position into mesh with the worm unless the notch (20) in disk 1 is engaged by the brass extension of the solenoid armature (17). The circuit through this solenoid is closed by the contact, *L*, of the recorder. The brass extension of the armature of a second solenoid (18) engages a notch (19) in the disk 3, to hold open the stopcock, *b*, whenever the recorder potential falls far enough to open the contact, *H*, of the recorder. The gear, 10, is driven continuously and operates the rocker, 6, to open the stopcock, *c*, at regular intervals. Disks 1 and 2 make one revolution in about 10 seconds. The rocker arms, capillary, and supply level are usually adjusted to give 1 or 2 drops whenever a stopcock is opened. These adjustments may easily be varied, however, to give anywhere between about 5 to 8 openings for each drop and 10 to 15 drops for each opening.

The arrangement of the amplifier and potentiometer is indicated by Figure 3.

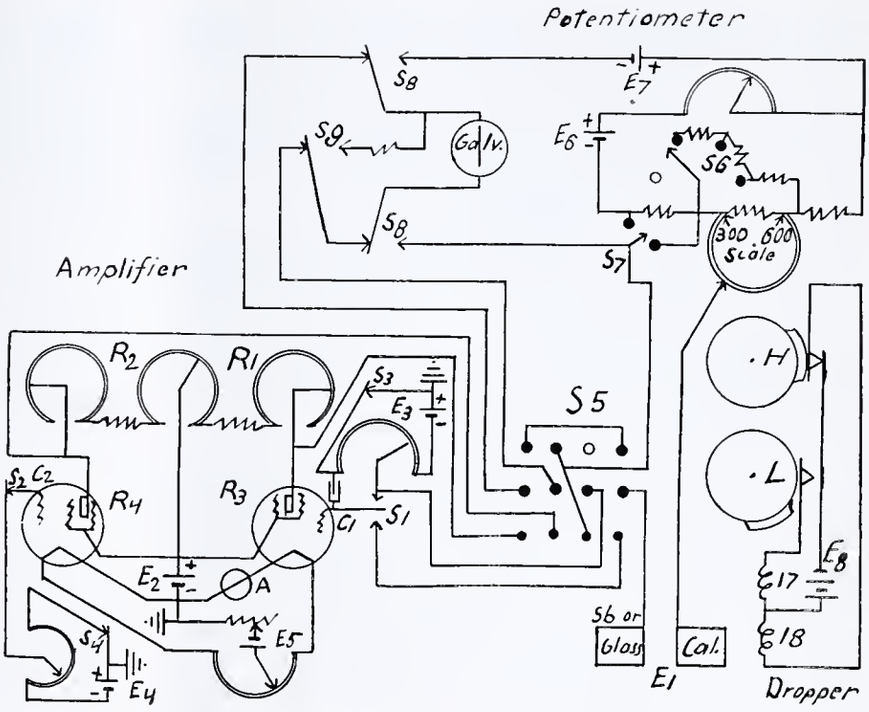

FIGURE 3. ARRANGEMENT OF AMPLIFIER AND POTENTIOMETER

A.	Ammeter for filament current
E_1.	Potential to be measured
E_2.	*B* battery of amplifier
E_3, E_4.	Batteries and potentiometers for holding *C* grids of amplifier at free potentials
E_5.	*A* battery of amplifier
E_6.	Working cell of potentiometer
E_7.	Weston cell for standardizing potentiometer
E_8.	Battery or power-line connection for operating solenoids
H, *L*.	High and low contacts for control mechanism
R_1, R_2.	Wire resistances of amplifier bridge
R_3, R_4.	Tube resistances of amplifier bridge
S_1, S_2.	Switches to make or break contact with *C* grids of R_3 and R_4
S_3, S_4.	Switches for opening and closing circuits supplying *C* bias
S_5.	Four-pole double-throw switch to enable use of amplifier when closed down and to enable use of potentiometer without amplifier when closed up
S_6.	Selector switch for adjusting range of potentiometer
S_7.	Selector switch for adjusting zero of potentiometer scale
S_8.	Switch for standardizing potentiometer
S_9.	Motor-driven tapping switch for testing balance of bridge
17, 18.	Coils of solenoids shown in Figure 2

EXPERIMENTS

Three records of controlled e. m. f. are shown in Table I. Each of these records is typical of at least four experiments under similar conditions. The longest experiment, A, was made while neutralizing the acidity developed in 1.5 liters of milk. This acidity was developed by lactic fermentation and was neutralized with 2 *N* sodium hydroxide. The controlled stopcock, *b*, of Figures 1 and 2, opened whenever the e. m. f. of the calomel-antimony cell was below 350 mv. During the first $1^1/_3$ hours, the regular stopcock, *c*, was being used in addition to the controlled stopcock, *b*. This accounts both for the unusually rapid rate of addition shown in Table I, and also for the fact that the e. m. f. of the fermenting mixture was carried 3 mv. too high. For the remainder of this experiment, stopcock *c* was kept closed. After closing stopcock *c* the e. m. f. did not vary more than about 1 mv. After $12^3/_4$ hours, the fermentation

TABLE I. RECORDS OF CONTROLLED ELECTROMOTIVE FORCE

Experiment	Time	Sol. per Min.	Dropper Operated	Electrode Potential: Quinhydrone	Electrode Potential: Controlling Mean	Electrode Potential: Controlling Variation
	Hr.:Min.	*Gram*		*Mv.*	*Mv.*	*Mv.*
Record A		2 *N* NaOH			Antimony electrode	
	0:25	.....		...	350	.
	1:19	0.655	Continuously except for one 2- or 3-minute period in each half hour	...	353	1
I	1:25	.....		234 (milk)	...	.
	1:30	.....		...	350	1
	6:08	0.245		...	350	1
II	7:00	.....		224 (milk)	...	.
	10:50	0.039	Only for 2- or 3-minute periods at increasing intervals	...	350	1
	12:45	0.00087		...	350	1
	16:15	0.00047			350	1
III	16:21	.....		213 (milk = pH 6.15)	...	.
IV	16:23	.....		263 (buffer of pH 7.00)	...	.
	17:41	0.248	Continuously except for last 10 minutes	...	375	.
V	17:44	.....		255 (milk = pH 6.85)	...	.
Record B		10 *N* NaOH			Antimony electrode	
	1:40	.....	Continuously except for seven periods of 1 minute each		540	Extremes 20
	1:53	0.081			550	Usual 5 to 10
	3:11	0.101	Very short periods at 3- to 4-minute intervals		553	All above
	4:32	0.046			557	operating
	6:27	0.055	Somewhat longer periods at 5- to 6-minute intervals		550	potential
Record C		10 *N* NaOH			Glass electrode	
	9:02	.....			...	.....
	9:20	0.083	For periods usually less than 1 minute at intervals of about 3 minutes		415	From about 25 below to between 20 and 50 above operating potential
	9:37	0.082			408	
	9:53	0.081			401	
	10:08	0.086			408	
	10:45	0.086			402	

was nearly completed as shown in Table I, by the sharp fall in the rate at which alkali was added. The recorder was therefore stopped for $3^1/_2$ hours to further prove the end of the reaction. The recorder was then restarted and set to add alkali until the e. m. f. should reach 375 mv. and the fermented milk become nearly neutral. Enough alkali to produce this effect was added in about $1^1/_4$ hours or when the experiment had run $17^1/_2$ hours.

Since the antimony electrode is not reproducible and is somewhat unreliable, and since the quinhydrone electrode is frequently used to measure the pH of milk, the controlling cell was compared with a quinhydrone cell. At four points, I, II, III, and V, the pH of samples of the fermenting milk were measured in a cell consisting of two quinhydrone electrodes. One of these electrodes contained a buffer of pH 2.58 and the other a sample of the fermenting milk. Between the last two of these readings at point IV the quinhydrone cell was calibrated by replacing the electrode containing milk with one containing a buffer of pH 7.00. The potentiometer recorded the calculated e. m. f. of 263 mv. The change on the quinhydrone electrode from 213 mv. at III to 255 mv. at V, or a change of 0.70 pH units, represents a change from 350 to 375 mv. on the antimony electrode. The 1 mv. variation in controlled e. m. f., therefore, represents a variation of about 0.028 pH unit.

The second experiment, B, was made while neutralizing with 10 *N* sodium hydroxide, the acid formed during methylation of lactose. In this experiment, the controlled stopcock opened whenever the e. m. f. of the calomel-antimony cell was below 550 mv. Before any addition of alkali, this methylating mixture contained 30 grams lactose, 50 cc. water, and 125 cc. dimethyl sulfate. The antimony electrode was probably at least as sensitive here as in record A. It is difficult, however, to make satisfactory comparisons with either colorimetric or electrometric indicators in such a complicated and concentrated system.

The third experiment, C, was made while methylating glucose in concentrations similar to those used for lactose. The glass cell and amplifier were employed for this experiment. The controlled stopcock opened whenever the e. m. f. was below 400 mv. A calibration of this cell was previously obtained by noting that its e. m. f. changed from 463 to 410 mv. when the cell was transferred from a buffer of pH 8.23 to one of pH 7.58. Since the e. m. f. of this record showed large regular variations, mean values over convenient time intervals were determined with the aid of a planimeter. The much more uniform rate at which alkali was added in record C as compared with record B is shown in Table I. The explanation may be that the e. m. f. of the antimony electrode is influenced by other things as well as pH, while the glass electrode is specific for, and quickly responsive to, changes in pH.

Summary

An electrometrically operated buret has been described which does not discard samples of the controlled mixture and does not introduce appreciable quantities of foreign substances. The action of the buret is sufficiently precise to permit the use of a very concentrated solution for controlling the e. m. f. of the reaction mixture.

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Use of Pump as Gas Sampler

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In the study of small changes in the composition of chamber air, involving the analysis of gases to 0.001 per cent, the Nutrition Laboratory has found it convenient and almost necessary to have a gas sampler, holding a volume sufficient to permit analysis to be made in duplicate or even triplicate, that will store the gas, when dry, for a period of 24 hours without a measurable change in the composition of the gas. For this purpose this laboratory has adapted a plunger pump, described by Benedict and co-workers (*1*, *2*, *3*), to which is attached a capillary three-way stopcock. Storage of gas in a modification of this pump makes it possible to obtain remarkable agreement of results in analyses of a gas sample on two or more gas-analysis apparatus and duplicate analyses on the same apparatus. Moreover a sample can be stored in the pump for 24 hours, and its composition will remain unchanged.

This pump has several distinct advantages over the common gas samplers. Since it is made of metal, it is less fragile than glass. Owing to its ingenious mechanical construction, it is capable of propelling gas in and out with certainty that there is no contamination of the sample. It does not use mercury. It has a capacity of 370 cc., permitting at least three 50-cc. samples of the gas even if the "washing" method of sampling is used. A mercury sampler of this capacity would have a tremendous weight. It can be set down on any flat surface, thus eliminating the need of a special holder at all times as required by the Haldane (*5*) sampler. A simple rack has been found convenient to hold the pump while transferring the sample into a gas-analysis apparatus.

Description

The pump consists essentially of a cylinder *C* with an air-tight piston. The cylinder is a seamless drawn brass tube of No. 20 gage (Stubbs), 22.86 cm. in length, having an inside diameter of 4.84 cm. This cylinder is soldered into a machined brass casting *J*, which is threaded to screw into a 6.4-mm. (internal diameter) pipe tee, *K*. This joint is also soldered. A tapered brass tube *H* is soldered into the side of the tee. One side of a three-way glass stopcock *G* is connected by a piece of rubber tubing to this tapered tube. The lower side of the tee is closed by a threaded brass rod, soldered into the tee. The rod in turn screws into a 10 × 15 cm. cast-aluminum base *P* which serves as a stand for the pump.

The piston of the pump is the unique feature, which, by obtaining an air-tight closure, makes the pump available for gas storage. The piston and rod are made in two sections. One section consists of a 26-cm. length of 6.4-mm. steel rod *A* which is screwed and soldered into the center of a 5.08-cm. brass disk *B* 3.2 mm. thick, having its edge beveled at 45°. A nut is also screwed onto the end of the rod, to insure rigidity. The opposite end of the rod is threaded for a short distance and has a slot in it to permit turning the rod with a screw driver. The other section

is a 3.2-mm. brass pipe D 23.83 cm. long, which is soldered into the center of a disk E of the same diameter and thickness as the other disk but with the bevel on the opposite side. The center of this second disk is drilled out to the size of the inside of the brass pipe and through this pipe the rod A passes. The two beveled disks E and B will form a V-shaped section. Into this space a circular leather washer W with a V-shaped, or triangular, cross section is placed. This washer is made from a 6.4-mm.

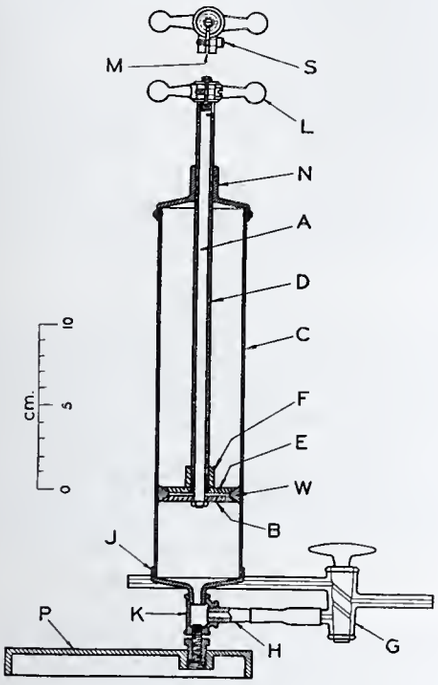

Figure 1. Details of Pump Used as Gas Sampler

tbick leather disk, 4.85 cm. in diameter, by starting on each side 2 mm. from the circumference and cutting towards the center at a 45° angle. By screwing the handle L on farther, the two brass disks are drawn closer together, which causes the bevels to push the leather washer out tighter against the wall of the cylinder. Thus, it is possible to secure a tight closure. The handle L is a machined brass casting that has been tapped to fit the thread on the steel rod. The slot M with the aid of a set screw S permits locking the handle in any position desired. The cap N is a machined brass casting. It is fastened by two screws to the top of the cylinder and serves as a guide for the piston rod. The spacer F is used as a stop for the upward stroke. The stroke of the pump is 200 mm., which produces a displaceable volume of 370 cc. By regulating the length of the spacer F and the length of the guide N, the stroke of the pump can be made an exact length.

In transferring the gas from the pump into a gas-analysis apparatus a stand with a rack to propel the handle is used (Figure 2).

Preparation for Use

To insure 24-hour storage of a sample of gas in the pump without change in composition, the pump should be thoroughly cleaned and dried. The pumps used in obtaining the results given in this article were prepared in the following manner:

The entire pump together with its leather washer, excepting the stopcock, was thoroughly washed with benzine to remove all traces of grease, oil, and dirt. The pump was finally rinsed in clean benzine and dried by standing in air until all traces of benzine were removed. This required 4 to 8 days, and in some cases it was necessary to complete the drying in an oven. The washers received especial attention to remove all tannin residues and oils. These were then soaked in melted white vaseline for several days until they were thoroughly pliable and well impregnated with this grease. The pumps were then reassembled.

The pumps were next tested for tightness of the piston at all positions. This is accomplished by connecting a glass tube (about 12 cm. long) by rubber tubing to the stopcock, which is turned to the pump. The pump is filled with air and the glass tube is then placed in a glass containing approximately 5 cm. of water. By forcing the handle down a short distance and holding it by the thumb and forefinger, to prevent moving, a small quantity of gas is ejected and the air will fill the tube to the bottom. If the air remains at the bottom of the tube for a half minute, this point of closure of the piston may be considered tight, another small quantity of air may be ejected by forcing the handle down somewhat farther, and the test made at this new position. If a portion of the pump is found that does not hold this 5 cm. of water pressure, which will be shown by water rising in the tube, the handle is turned so that the washer is slightly tightened against the wall of the cylinder, the pump filled with air, and the testing recommenced.

A pump once dried in the manner described will continue so indefinitely if only dry air is drawn into it. With normal care pumps stay tight for reasonable periods without adjustment.

Results of Tests

To demonstrate the limits of accuracy in duplicating an analysis of gas from the sampler, using the same apparatus for the duplicate analysis, a group of pumps was filled with gas obtained by burning ethyl alcohol in a current of pure outdoor air at such a rate that the carbon dioxide content of the resulting gas was approximately 1 per cent. These samples were analyzed on the Carpenter (*4*) gas-analysis apparatus twice the same day (approximately 3 hours apart)

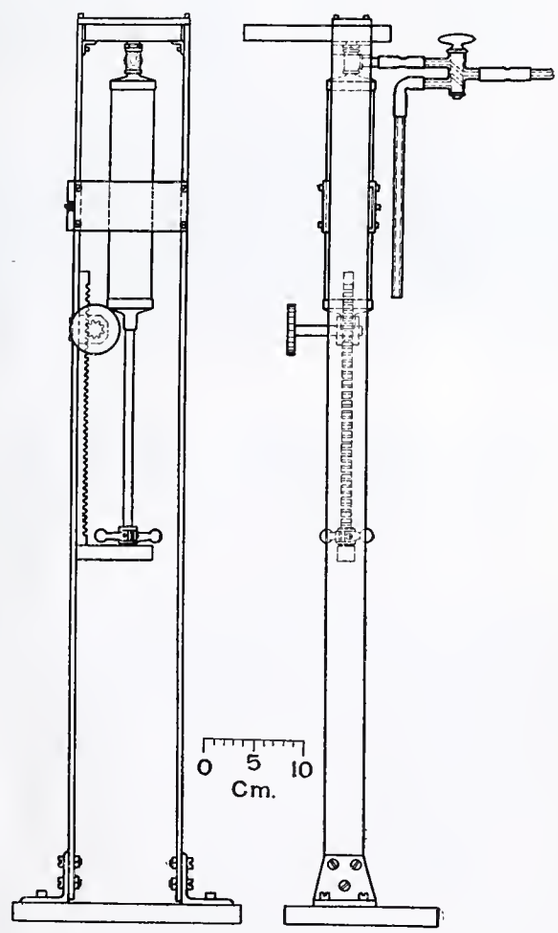

Figure 2. Pump Rack to Hold Pump in Inverted Position

Rack and pinion to facilitate compression of gas for transfer of sample into gas-analysis apparatus

on the same instrument. In a series of 23 samples the average difference in results was 0.002 per cent for carbon dioxide and 0.004 per cent for oxygen. The maximum difference for carbon dioxide was 0.013 per cent and for oxygen 0.010 per cent.

Another series of 10 samples was analyzed on two different gas-analysis apparatus to show the effect, if any, of using different apparatus. In this series the average variation

between the pairs of analyses was 0.004 per cent for carbon dioxide and 0.004 per cent for oxygen, with a maximum difference of 0.014 and 0.010 per cent for carbon dioxide and oxygen, respectively.

Table I. Results Obtained from Analyses of Samples in 24-Hour Storage Test in Pumps

Pump No.	Day of Analysis	Gas-Analysis Apparatus No.	Carbon Dioxide %	Oxygen %	Resp. Quotient
2	First	112	1.036	19.534	0.665
	First	38	1.032	19.537	0.664
	Second	112	1.030	19.535	0.661
3	First	38	1.025	19.546	0.663
	First	20	1.028	19.548	0.667
	Second	38	1.022	19.545	0.660
6	First	38	1.061	19.494	0.663
	First	112	1.061	19.513	0.673
	Second	38	1.058	19.498	0.662
9A	First	38	1.031	19.546	0.666
	Second	38	1.034	19.539	0.667
10A	First	112	0.936	19.674	0.666
	Second	112	0.914	19.703	0.662
11	First	38	0.861	19.791	0.674
	Second	38	0.858	19.789	0.669
14A	First	20	0.933	19.669	0.660
	First	38	0.933	19.675	0.664
	Second	38	0.924	19.680	0.659
16	First	112	0.921	19.699	0.668
	Second	112	0.922	19.699	0.670
17	First	38	0.887	19.744	0.666
	Second	38	0.886	19.749	0.669
18	First	20	0.928	19.690	0.669
	Second	38	0.923	19.689	0.663
22	First	112	0.891	19.743	0.670
	Second	112	0.890	19.743	0.669
23	First	112	0.947	19.667	0.670
	Second	112	0.947	19.662	0.667

Each pump that was proved tight and had been previously dried was then tested to determine if it would store a sample of gas overnight (approximately 24 hours) without appreciable change in the composition of the gas. The pumps were filled with a gaseous mixture obtained as described above. In one trial the samples were not completely dried. Duplicate analyses on the same day agreed well, but on the following day every carbon dioxide percentage was lower (average 0.027 per cent), whereas the oxygen percentage remained nearly the same in half the pumps and increased by a small amount in the rest.

On repeating this 24-hour storage test on 12 pumps with the gas thoroughly dried, the carbon dioxide percentage on the second day averaged 0.004 lower than the first day, whereas the average oxygen percentage increased 0.002. The results of this test are tabulated in Table I. Pump 10A was not considered satisfactory. When a sample was stored overnight in pump 10A in a later test, an analysis on the second day gave percentages for both carbon dioxide and oxygen that agreed within 0.001 with the results obtained on the previous day. Thus these pumps, if clean, dry, and air-tight, will store dry gas for approximately 24 hours without detectable change in composition of the gas.

Summary

A metal pump, which is less fragile than glass, does not use mercury, can propel gas itself, has a capacity of 370 cc., and can be easily handled, has been adapted as a gas sampler. When clean, dry, and air-tight it will store dry air approximately 24 hours without measurable change in carbon dioxide or oxygen percentage. With this sampler it is possible to duplicate analysis of air on the same or different apparatus and a series of such analyses shows good agreement.

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Determination of Ethyl Alcohol in Gasoline-Alcohol Mixtures Using a Zeiss Immersion Refractometer

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The increasing demand that alcohol, made from farm products, be added to gasoline makes desirable the development of a method for the determination of the amount of alcohol present in such mixtures. The following procedure permits determinations with an average deviation of 0.2 per cent of the amount of alcohol present.

Known mixtures containing 2.5, 5, 7.5, 10, and 15 per cent, by volume, of anhydrous ethyl alcohol in gasoline were prepared. All measurements were made with burets, using 50-cc. samples for the analysis. Each sample was placed in a glass-stoppered graduated cylinder and 25 cc. of distilled water were added. The contents were then shaken thoroughly in order to have the two layers come to a state of equilibrium. The water layer was drawn off from each sample and the refractive index was determined at 20° C. by the use of a Zeiss immersion refractometer. Solutions were made from the regular gasolines of Texaco, Phillips "66", D-X, and Deep Rock, respectively. Also some completely denatured alcohol (Formula 188) was dehydrated and mixed with Deep Rock gasoline, to find effect of denaturants upon the readings.

The results obtained are shown in Table I. It will be observed that the refractive indices obtained from each of the types of basic gasolines, even when denatured alcohol is used, agree very closely. From these data the mean values of the refractive indices were determined and can be plotted against the per cent of ethyl alcohol by volume.

Using these data a graph may be drawn, from which the per cent of ethyl alcohol present can be read directly.

Table I. Refractometer Readings

Types of Gasoline	0% Alcohol	2.5% Alcohol	5% Alcohol	7.5% Alcohol	10% Alcohol	15% Alcohol	Sp. Gr.
Texaco	15[a]	20.5	26.2	32.4	37.8	48.3	0.728
Phillips "66"	15	20.5	26.2	32.4	38.0	48.3	0.712
D-X gas	15	20.9	27.0	33.0	38.3	48.5	0.724
Deep Rock	15	20.5	27.0	32.8	38.3	49.0	0.731
Deep Rock and completely denatured alcohol	15	20.5	27.5	32.6	38.2	49.0	...
Average readings	15	20.6	26.6	32.6	38.1	48.5	0.724

[a] The refractometer was set to read 14.5 in distilled water.

Method of Analysis

Measure exactly 50 cc. of gasoline-alcohol solution into a glass-stoppered separatory funnel. Add 25 cc. of distilled water, shake the contents thoroughly to bring the two layers to a state of equilibrium, and draw off the water layer. Determine its refractive index at 20° C. by means of the Zeiss immersion refractometer.

Received April 27, 1933.

A Simple Automatic Water Still

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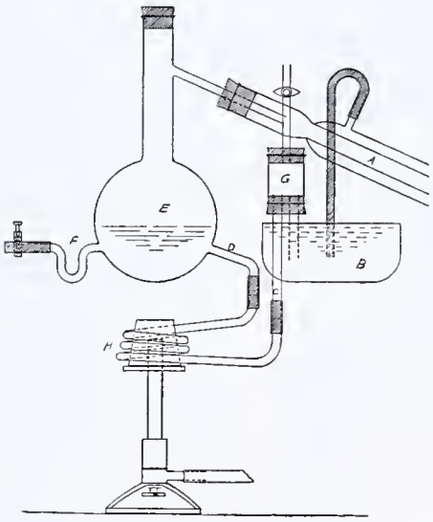
IT OFTEN happens that a worker in a small laboratory feels that he can hardly afford to purchase an automatic still of the usual type, yet the need for distilled water is imperative and the use of a still which is not automatic consumes more time than is justified. The simple, inexpensive still shown in the accompanying sketch should prove helpful in a small laboratory, or in a larger laboratory when the large still is out of order.

This still may be made from a 500-ml. distillation flask by sealing two additional side tubes near the bottom of the flask, as shown in the sketch. In operation the set-up of the still is essentially as indicated. The water from the condenser, *A*, flows into a small water bath, *B*, the overflow from which is connected with the sink. A siphon, *C*, is connected with the second side tube of the still, *D*, and serves to keep the water in the bath and the still, *E*, at approximately the same level.

As distillation progresses some water must be drawn from the still to prevent excessive concentration of dissolved material. For this purpose a third side tube, *F*, is provided. If no temporary hardness is present the tip of *F* may be drawn down to a jet of such size as to permit the outflow of water at the rate desired. In the presence of temporary hardness the outflow may better be regulated by means of a rubber tube and screw-cock as shown. This avoids clogging of the glass jet by precipitated solids and permits flushing to remove solids by merely loosening the cock. An air trap, *G*, should be used to prevent air dissolved in the feed water from collecting in the siphon and interrupting its action.

A considerable increase in efficiency of operation results from the use of the preheater, *H*. This may be made of 10-mm. copper tubing, coiled as shown around the top of the burner. Care must be taken that all parts of this coil slope upward toward the still, so that the heated water (and steam) will rise to the still instead of tending to move in the opposite direction. Of course the efficiency of the still may be further increased by wrapping the flask with asbestos paper.



Automatic Water Still

To secure smooth boiling, scraps of porous porcelain or boiling tubes may be used. The former are to be preferred if either side tube *D* or *F* is attached very near the bottom of the flask, since in this case the boiling liquid tends to throw the light boiling tubes into the opening of the side tube.

Received June 21, 1933.

An Adjustable Temperature Regulator

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A SIMPLE adjustable temperature regulator which has been very successful in this laboratory for the past two years is shown in Figure 1. This regulator can be constructed readily from the common type of regulator which accompanies any Freas thermostat. It consists of a large mercury reservoir *A* with a side tube *B* of uniform bore. The side tube is fitted with a brass cap through which is threaded a nickel rod carrying a tight-fitting rubber plunger. The brass cap is cemented to the side tube with de Khotinsky medium cement. By raising or lowering this plunger the height of the mercury at *C* can be varied at will. This device, which eliminates the necessity of adding or removing mercury from the regulator every time the temperature is changed, is of particular value in the determination of the temperature coefficients of galvanic cells. In this connection this regulator has been used from 0° to 30° C. at 10° intervals. The desired temperature was maintained to ±0.02° C. A larger temperature range is possible if desired.

The thermostat liquid (at 0° a mixture of alcohol and water was used; at the other temperatures pure water) was cooled by circulating calcium chloride brine through cooling coils arranged around the sides of the bath. Slightly more cooling than necessary was employed so that the desired temperature could be maintained by regulating the heat supplied by electric heater units. The brine was maintained at a temperature of approximately −15° C. in an insulated tank by a large Frigidaire compressor and evaporator. The brine was circulated by a pump and the quantity needed for the various temperatures controlled by suitable valves, which were so arranged that a varying number of cooling coils could be used in the bath.

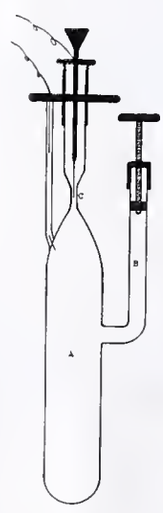

Figure 1. Adjustable Temperature Regulator

For operating the thermostat successfully below room temperature, both caps of the regulator must be tightly sealed with paraffin to prevent condensation of moisture within the side arm and at the mercury contact surface at *C*. The regulator was used in conjunction with a relay switch, such as described by Beaver and Beaver[2] with very satisfactory results.

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[1] Present address, Rhode Island State College, Kingston, R. I.

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Microabsorption Spectra

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In the study of rare earths frequent use is made of absorption spectra to detect the presence of members of the group and to determine the purity of materials. Satisfactory absorption spectra of small amounts of liquids may be made by using a glass capillary tube as the solution container and passing light longitudinally through the liquid. Capillary tubes for such use must be straight and thin walled. Ordinarily used methods do not produce satisfactory tubing. However, by using a specially designed electric furnace, satisfactory tubing can be made.

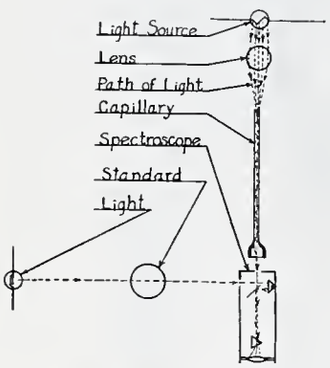

Diagram of Apparatus

The furnace was made by wrapping a short length of 10-mm. soft glass tubing with asbestos paper. Six turns of nichrome wire were wrapped around the tubing and paper, with about 1-mm. space between turns. The wire was covered with several coats of alundum cement, ample time being allowed for drying each coat before the next was applied. After the last layer of cement was dry, it was wrapped with asbestos paper, which, in turn, was wound with asbestos cord. The ends of the nichrome wire were connected with an electrical circuit which was allowed to flow until the furnace became red hot inside. The current was then turned off and cold water was poured into the red hot, soft glass tube. In this way the glass was shattered, facilitating its removal with a bent wire. The furnace was now ready for use.

If the furnace is set up in a vertical position, and a piece of 3- to 8-mm. glass tubing suspended down through the center of it, a very straight capillary may be made by allowing the furnace to heat up and soften the glass. The glass will draw itself out by its own weight and drop vertically. When the glass has cooled, it should be cut so that it will give a capillary and tubing about 5 cm. in length. The tube is cleaned and silvered in the usual manner and the silver removed from the inside.

Since the opening of the capillary is very small, it does not allow a large amount of light to enter the solution, and thus gives rather poor results at the spectroscope. This difficulty is eliminated by using a very bright source of light and a line focus lens. The lens is so adjusted that the line focus is parallel to the slit in the spectroscope, and lies just inside the end of the capillary. The line focus lens consists of a clear glass test tube full of water or carbon disulfide.

The spectroscope used with this apparatus is the direct-vision instrument which is equipped with a comparison prism. This construction permits the comparison of two spectra in the same field. In this way the intensity of the absorption bands in a solution under examination may be intimately compared with that of the bands in a standard solution. Photographic records may be made if desired.

The sample of the unknown is dissolved in a minimum but known volume of solvent, usually about 2 cc., and a known amount is placed in the capillary. By comparison with the spectra of a series of standard solutions the analysis of the unknown may be made. The apparatus is set up as indicated in the diagram.

This set-up was used in a study of the separation and purification of neodymium and praseodymium, and was capable of detecting 0.00005 gram of neodymium. It is quite true that other spectroscopic methods are more sensitive, but they are more complicated and involve loss of the sample. A polished platinum capillary might be substituted as a modification of this apparatus.

The apparatus can be used in studying the absorption spectrum of any soluble substance, and is especially useful in rare earth work.

Received July 3, 1933.

An Air Trap for Water Lines

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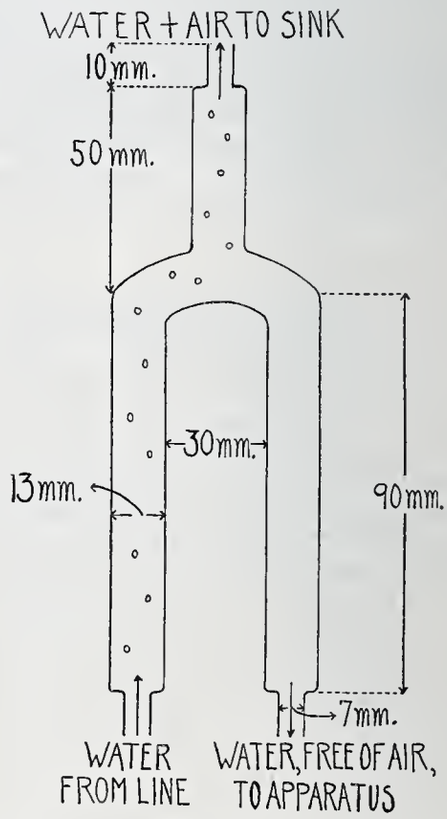
In the course of some experiments requiring rapid dialysis, use was made of a modification of the concentrating dialyzer (*2*) devised by F. E. Kendall (*1*) of the College of Physicians and Surgeons and Presbyterian Hospital, New York, N. Y. It was noticed, however, that the air carried in the water line invariably emptied the vessel overnight, thus slowing up the process. In order to overcome this drawback a trap was devised which effectively removes the air.



This simple piece of apparatus can be used wherever a constant stream of water, free of air, is required. The only precaution is that the water must run in sufficiently fast so that it is constantly flowing through the arm leading to the sink, as well as that leading to the apparatus.

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HARRISON E. HOWE, EDITOR

Measurement of Tube Wall Temperatures in Heat Transfer Experiments

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DETERMINATION of the temperature of tube walls is an integral part of most experimental work involving a study of heat transfer coefficients to and from these surfaces through the enveloping films. The final degree of accuracy obtained in such work is usually controlled by the accuracy of determination of the surface temperatures.

Recent important investigations concerning the condensation of vapors and heating of liquids have required more than an approximate knowledge of the wall temperatures of the experimental tubes. Some few investigators, justified by accepted data, have preferred to assume approximate heat transfer coefficients for one or another of the films rather than to carry out the work necessary for the actual measurement of the desired temperatures. Others have adopted or developed methods that have not eliminated this part of heat transfer studies as a source of considerable error. The amount of error involved in any given case can only vaguely be estimated, but it is certain that a better correlation of all such work would be possible with improved methods of measurement.

Reviews of the methods utilized have recently been made by Othmer and Coats (*8*) and Colburn and Hougen (*4*). Additional references supplementing these are included in this paper. Installations as applied to tubes alone are considered.

By far the major portion of the work done on this problem has been carried out with thermocouples, which, because of their inherent economy and flexibility of installation, may be considered the most likely instrument to be chosen. Installations of resistance thermometers (*3*, *7*), mercury thermometers (*2*), portable contact recorders (*1*, *5*), and extensiometers (*9*, *10*) have been made. These latter methods are not generally applicable and are not to be preferred if a successful thermocouple method is an alternative.

USE OF THERMOCOUPLES

Any installation involving thermocouples should meet the following requirements:

1. The temperature recorded by any given junction must be that of the corresponding wall temperature or one from which the wall temperature may be calculated by the use of known relations.
2. The effect of heat conduction to the junction by the leads should be minimized or eliminated.
3. The characteristics of the normal film on the wall must not be disturbed by the installation.
4. Any installation should be in mutual agreement between different couples and should be capable of accurate reproduction.
5. The assembly should be sufficiently rugged to withstand all conditions encountered during installation of the tube in the test apparatus.
6. A minimum of time should be required for installation and calibration unless the permanency of the set-up warrants additional work.
7. Frequent recalibration and attention to the couples should not be necessary.

As most investigations are carried out with tubes of relatively small diameter and of considerable length, mechanical considerations will restrict the operator to the use of the outside wall of the tube. When it is necessary to contend with a vapor condensing on this wall, the problem of an undisturbed film becomes paramount, particularly with vapors of large latent heats which form very thin films of condensate. Since relatively large temperature differences occur through these thin films, any mechanical imperfection or deformation of the natural surface in the vicinity of the couple junction that causes a penetration or distortion of the film will result in abnormal heat conduction to the junction (peened, plated, and slotted installations). If the lead wires from the junction are carried out directly into the higher temperature of the vapor space, the effect of heat conduction along the leads becomes considerable (peened and plated installations). There is no way at present by which this effect can be calculated.

No single thermocouple method developed to date, on the basis of data presented, can be said to be free from either or both of these objections, with the possible exception of the Kraussold installation (*6*).

The latter utilizes a longitudinal groove [0.0625 inch (0.16 cm.) deep, 0.125 inch (0.3 cm.) wide, and 6 inches (15 cm.) long]

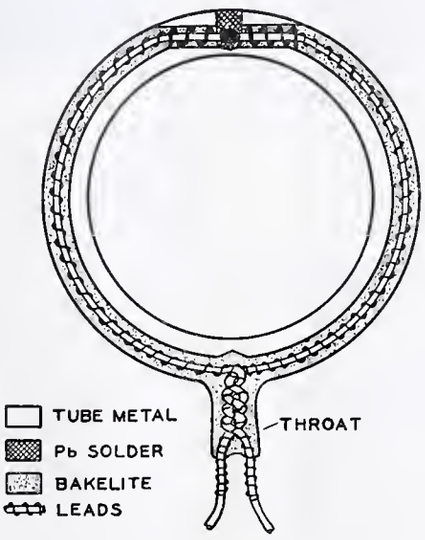

FIGURE 1. THERMOCOUPLE INSTALLATION

[1] Present address, Dow Chemical Co., Midland, Mich.

milled in the tube wall. A spline of the tube material, made with a concave bottom to allow for the couple and leads, is cut to fit the groove snugly. When the spline has been driven into place an equivalent of the original surface remains. The leads are brought through the film at opposite ends of the spline and well away from the junction. It has been found extremely difficult to make even a passably good job by this method. Even if a smooth external surface is obtained, the spline has a tendency to work loose on repeated heating and cooling. Further, the leads in the Kraussold method disturb the drainage of the condensate if the tube is vertical. It is only necessary to try the Kraussold method and the one here suggested to decide which is superior.

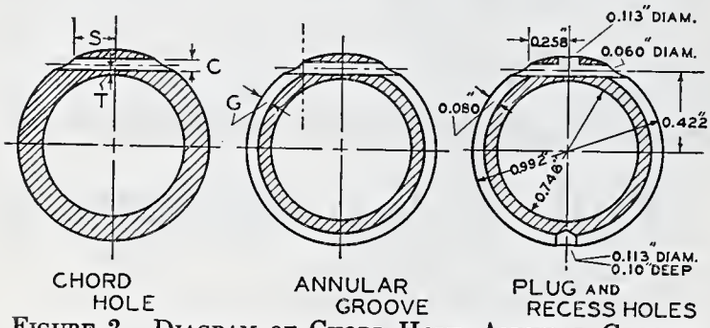

FIGURE 2. DIAGRAM OF CHORD HOLE, ANNULAR GROOVE, AND PLUG AND RECESS HOLES

Dimensions are for installation in 1-inch 11-gage tube.

The solution to both the requirements of unchanged surface conditions and freedom from abnormal heat conduction to the junction may be reached in a logical fashion. The couple junction should be placed under a surface over which the film drainage is not disturbed, and the leads must be withdrawn for an appreciable distance from the junction through a section of the wall that is isothermal with the point at which the couple is embedded.

PROPOSED METHOD

Reference to Figure 1 will illustrate the features of the method. The thermocouple is inserted in a hole drilled through a chord of the wall, and the leads are carried around the tube in an annular groove to be withdrawn at the back, 180° from the junction. The junction itself is brought into metallic contact with the wall by solder admitted through the plug hole above. Bakelite cement of special composition provides electrical insulation and fills the groove and chord hole up to the junction. The excess solder and Bakelite may be removed with fine emery cloth to produce a continuous and polished surface at all points except where the leads leave the tube, 180° from the point of measurement.

It is necessary to employ tubes of somewhat heavier walls than those ordinarily used in order to provide sufficient metal for the chord drill, which is necessarily limited as to the smallest size that can be employed. The additional metal offers no disadvantage as it is only a very small part of the total resistance to heat flow, and transfer through it can be accurately calculated.

DETAILS OF METHOD

Steps in machining are as follows (Figure 2):

CHORD HOLE. Diameter of drill chosen is dependent upon obtaining greatest distance S without causing too small a thickness at T. Drilling is done with template shown in Figure 3.

ANNULAR GROOVE FOR LEADS. Width = C, depth = G. Cut on lathe with round-nosed tool of width = C (Figure 3). Lathe is moved by hand, lifting tool over uncut section.

PLUG AND RECESS HOLES. Diameter = approximately $2 \times C$ to a convenient drill size. Recess hole is necessary to permit proper footing for lead throat of Bakelite.

Thermocouples are made from copper-constantan of most convenient wire diameter. Junction is butt-soldered with silver to give neat bead that threads through chord hole.

INSTALLATION OF COUPLES. The plug hole is first tinned. The chord hole must be packed with asbestos thread during this operation. The couple is then threaded in. To center the junction and prevent sweating of solder into the chord hole while soldering the junction, short pieces of metal tubing, that fit closely over the leads and in the chord hole, are threaded over the leads and up to the junction. The tips of these tubes should be covered with melted borax to prevent solder from adhering to them. If hypodermic needles of proper size can be found, they are the most convenient type of tubing for the above work (D, Figure 3). The couple is soldered in, using a blast lamp to maintain the tube at the proper temperature. The solder must be allowed to flow naturally into the hole and must cool slowly. Ordinary lead-tin solder is recommended as satisfactory and most easily handled. When the couple is soldered in place, each lead is hand-wrapped in two steps (E, Figure 3): First, a cotton thread, of sufficient diameter to allow only slight clearance from the walls when well smeared with Bakelite, is wrapped around the portion of the leads in the chord hole, and well packed into the holes with the tubing previously mentioned. Lighter cotton is then wrapped around the leads from the holes and carried along a distance sufficient to provide for insulation in the groove and about one inch additional. A light coat of Bakelite is then laid in the groove and on the thread, and cured. Next, the leads are brought together at the recess hole, twisted around each other for about 0.5 inch (1.26 cm.), and then carefully bent or pushed into the very bottom of the groove at all points. With successive coats of Bakelite, the groove is completely filled and a throat of supporting Bakelite is built around the twisted leads. Excess

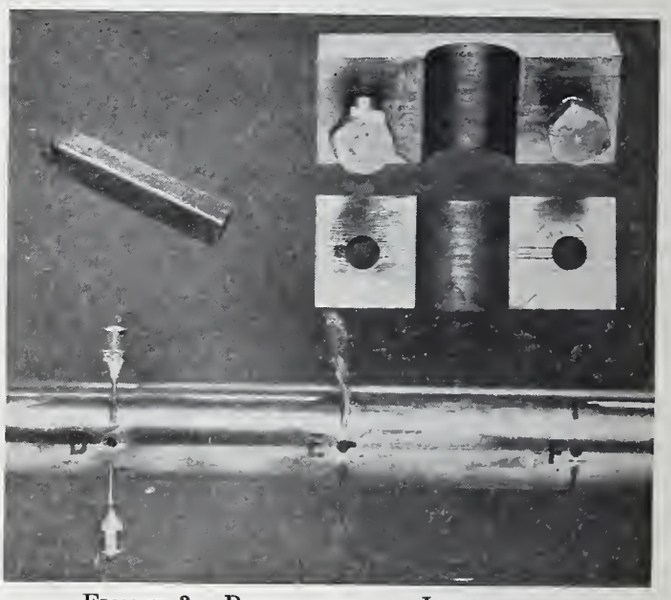

FIGURE 3. PHOTOGRAPH OF INSTALLATION

solder and Bakelite are removed, first with sand paper, and then with a fine grade of metallographic paper. The leads are joined to wires of similar composition, leading to the instruments, and proper insulation is applied to these joints. Thread and Bakelite will serve the latter purpose.

CURING OF BAKELITE. Bakelite resin BR-0013 has been found most satisfactory. This material should be mixed with kaolin or silica (200 mesh) in the proportions of two parts of resin to one part of filler. Better adhesion of the cured resin to the metal is obtained by use of the filler.

The material recommended will harden completely within 20 to 30 minutes at a temperature of 120° to 130° C. Thin coats must be applied. Curing the resin on the installations can most easily be effected by the use of an oven of special construction. This latter can be a transite box, split laterally and fitted with hinges. The ends are cut out to fit the tube

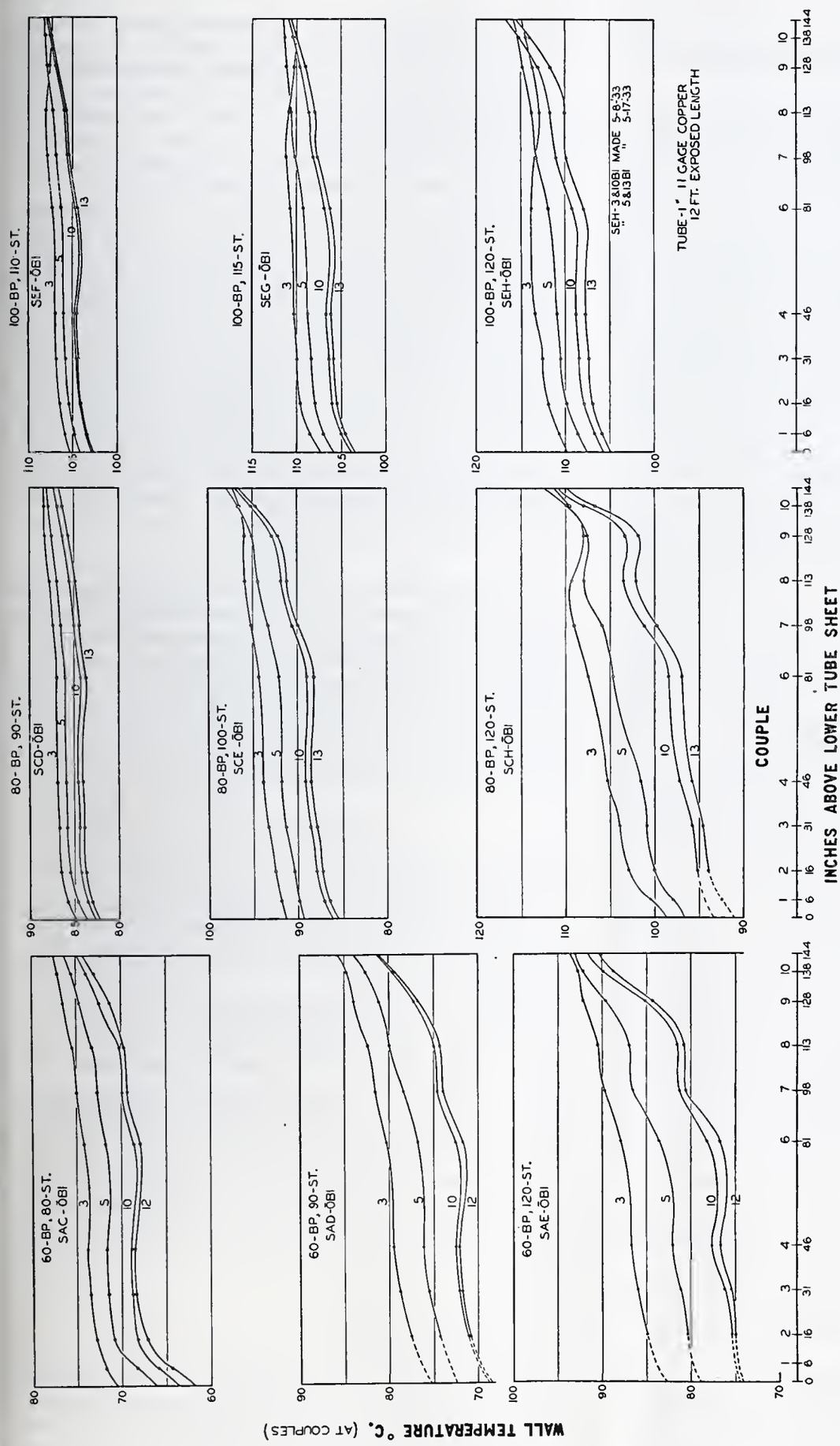

FIGURE 4. RESULTS ACHIEVED IN MEASUREMENT OF WALL TEMPERATURES

snugly. Sufficient coiled resistance wire is distributed on the inner walls of the box to maintain the desired temperature within the oven. Temperature control can be effected within the desired limits by additional series resistances. Radiation losses from the length of tube outside the box may be so high that it will be impossible to maintain a proper intensity of heat in the tube itself, and a longer period of time than is necessary will be required for curing. This difficulty may be overcome by the use of an internal heater for the tube, constructed of a short length of small-diameter iron pipe. The pipe is covered with an asbestos sleeve, wrapped with resistance wire, and then further covered with a spaced spiral wrapping of asbestos tape. This heating element is placed in the tube at a point under the junction. A moderate heat input will maintain the tube temperature at the same degree as that of the oven.

INSULATION OF LEADS THROUGH VAPOR SPACE. A satisfactory insulation of the leads through the vapor space is essential. Tests of various materials subjected to steam and hot water at temperatures of 250° to 280° F. (121° to 138° C.) for periods of 100 to 200 hours definitely proved that the usual forms of insulation are unsatisfactory. The insulations examined and found to be unsatisfactory include ordinary red rubber tubing, soft and lightly vulcanized black rubber, pure gum rubber, varnished cambric tubing (radio spaghetti), and enameled coverings. The form of insulation employed on R. C. fixture wire stood up best and suffered no apparent loss of insulating properties or any deformation. This type of covering was applied to the leads used in the investigations made in this laboratory and gave excellent service. No deterioration was found after more than 300 hours of exposure to saturated steam. These leads are flexible and may be brought out from the vapor space between flanged surfaces.

DATA FOR PRESENT INSTALLATION

Machining dimensions, see Figure 2.

Tubes: 1-inch 11-gage copper, 0.992 inch (2.5 cm.) outside diameter, 0.750 inch (1.9 cm.) inside diameter.

Thermocouple: Copper-constantan, No. 24 B. & S. wire, junction centered 0.074 inch (0.188 cm.) below outer wall.

Chord hole: No. 53 drill (0.0595 inch, 0.151 cm.).

Plug and recess holes: No. 33 drill (0.1130 inch, 0.287 cm.).

Bakelite: No. BR-0013, 2 parts, with 1 part 200-mesh kaolin.

Thread insulation: No. 20 cotton in chord holes, No. 60 cotton in grooves.

Grooves: 0.060 inch (0.152 cm.) wide, 0.080 inch (0.203 cm.) deep.

Hypo needles: No. 17 gage, 2 inch (5 cm.) length.

Experimental Application of Method

Preliminary trials were made in a small test apparatus which functioned as a single-tube horizontal water heater. Installations were then made on tubes of two forced circulation evaporators. Ten couples were installed on the tube of an experimental evaporator having one vertical tube 12 feet (3.7 meters) long, and six couples were installed on one tube in an eight-tube semicommercial forced circulation evaporator. Consistent results have been obtained with both installations.

Both of the above tubes were calibrated in a single-tube apparatus in which it was possible to maintain constant isothermal conditions at all points over the calibration range (30° to 120° C.) with a maximum variation of ±0.02° F. (0.01° C.). The known accuracy of calibration was ±0.001 millivolt (0.04° F. or 0.02° C.). Observed calibration values for the couples of each tube at any given temperature fell within a maximum range of 0.005 millivolt (0.18° F., 0.10° C.). Recalibration of the single-tube couples was made after 150 hours of operation. The values obtained did not diverge from the original results within the established limit of error, (0.005 millivolt = 0.18° F., 0.10° C.), and all couples were in the same relative agreement.

Results that have been achieved in the measurement of wall temperatures are well illustrated by Figure 4. This is a plot of the observed wall temperatures obtained with steam and distilled water in the 12-foot (3.7-meter) single-tube evaporator over a wide range of operating conditions. Actual couple readings, transferred to temperatures in ° C., are plotted against the locations of the couples on the tube. (No. 5 couple was damaged during the course of a repair job on the machine. No results for this couple are reported.) Each group of curves is representative of a fixed boiling point and steam temperature. Four different velocities of circulation were employed to give the several curves.

It is difficult to adduce positive evidence of the accuracy and reproducibility of wall thermocouples. The statements made above as to the reproducibility of the readings in calibration under conditions of no heat flow are not positive evidence of the behavior of the same couples when there is a temperature gradient through the tube and films. A study of Figure 4 will show, from the relative positions of the curves in all the groups, that the couples installed by this method are apparently giving dependable readings. This is borne out by the fact that all the groups show a similar change in the curves caused by a change in velocity. Stronger evidence (though still indirect) is the close correspondence of the curves for 10 and 13 feet (3 and 4 meters) per second. There would seem to be no error involved comparable with the accuracy of the work as a whole, when separate runs, often over a week apart and with many other runs made in the interval, will yield curves corresponding so closely as those for 10 and 13 feet (3 and 4 meters) in all the series, especially the series at 100° boiling point with steam at 110° and at 115° C.

With small over-all temperature drops only slight changes in wall temperature may be expected with changes in velocity. The curves for 80° boiling point, 90° steam, and 100° boiling point, 110° steam, indicate the close agreement that has been obtained. The very small decrease in wall temperature resulting from increasing the velocity from 10 to 13 feet (3 to 4 meters) per second for the latter set of conditions has been recorded accurately by the installed couples without a single overlapping value. Runs of the 100° boiling point, 120° steam, group were made on different days. The 3 and 10 foot (1 and 3 meter) velocities were completed a week before the 5 and 13 foot (1.5 and 4 meter) velocities were made. The 80 hours of operation conducted between those dates did not affect the consistency of the readings.

Comments

The method as developed and tested in this laboratory has proved very satisfactory. A modification of the manner of withdrawal of the leads from the tube has been found possible, so that, in a purely test apparatus, the tube and thermocouples with the leads consist of a compact unit. This will make feasible a study of the effect of tube surface conditions on heat transfer coefficients, a requirement of which is the constant observation and conditioning of the tube surface. A later report will consider the modification.

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Bumping Prevention

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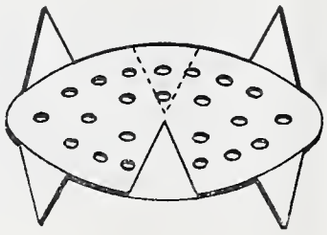
The author (*1*, *2*) has recommended the use of a porcelain sieve plate for preventing bumping, because it introduces no impurity and causes no oxidation. It is excellent for liquid boiled in a small round-bottomed vessel. For a thick layer of liquid, the plate is liable to rest on the bottom, cause overheating of the covered area, and result in the cracking of the vessel.



For the preparation of a large quantity of carbon dioxide-free water, the author has used successfully sieve plates made of sheet silver without cracking a single glass vessel in two years. For solutions that attack silver, the sieve plate could be constructed of platinum.

Literature Cited

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Quantitative Organic Microchemical Analysis in Industrial Problems

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MICROCHEMICAL methods deal, arbitrarily, with 1 to 10 mg. of material; such methods have been referred to by Emich as milligram methods to differentiate them from centigram or semi-micromethods and decigram or macromethods. This discussion will not include methods of chemical microscopy, which involve the application of the microscope to the solution of chemical problems, although they are of great value as research tools; Chamot (*6*) states that they offer even greater possibilities in time- and labor-saving than microchemical methods. Finally, discussion of highly sensitive identification reactions on organic and inorganic compounds and ions, spot tests, and spectroscopic, colorimetric, and nephelometric methods of analysis will be omitted altogether although these are justly included in the field of microchemical methods.

In the classification of quantitative microchemical methods of analysis there is the usual division into organic and inorganic branches. The technic for inorganic quantitative microanalysis has been carefully worked out, particularly by Emich and his co-workers, but the methods developed by Pregl for organic compounds appear to be receiving more attention. These methods are essentially the same in theory and practice as the older macromethods and have, in general, merely been improved and modified to permit using milligrams in place of decigrams.

Lavoisier is generally considered the founder of organic elementary analysis for, in 1781, he worked out an indirect gas-volumetric method of analysis by which he determined the composition of an organic substance from the products of its complete combustion to carbon dioxide and water and made clear the importance of elementary organic analysis to the science of chemistry. Minor improvements were made until, in 1830, Liebig and Dumas made the final improvements and developed the macromethod to practically its present form. With the exception of certain improvements suggested by Dennstedt in 1903 there were no important improvements in the technic of organic elementary analysis for carbon and hydrogen until the time of Pregl, a period of practically a hundred years.

The Dumas method for nitrogen appeared in 1883 and was improved by Schiff in 1886 by his development of the present form of azotometer. The period 1861–70 saw the development of the Carius method for sulfur and halogens, and in 1883 Kjeldahl published his method for the determination of nitrogen.

Development of Organic Elementary Microanalysis

In 1910 Pregl, in the course of a tedious investigation on bile acids, isolated a decomposition product which could be obtained only in extremely small amounts. He was faced with having to start anew with very large amounts of material or else to refine the methods of quantitative organic analysis so that he could get correct analytical results on previously unheard of small amounts of material which would lead with certainty to the empirical formula of his substance. Pregl was encouraged in deciding in favor of the second alternative by the success which Emich had attained in quantitative inorganic microanalysis.

By the end of 1911 the determination of carbon and hydrogen could be made on 7 to 13 mg. of organic material, even if nitrogen and small amounts of sulfur and halogens were simultaneously present; nitrogen could be determined either gasometrically or by titration, on 4 to 8 mg. of substance; and finally determination of sulfur and halogens could be made, also on 4 to 8 mg., by the method of Carius. In 1912 and 1913 many improvements were made, sources of error discovered and eliminated, necessary stringent conditions of technic imposed, time of analyses shortened, and finally the amount of starting material diminished to as low as 2 mg. New developments included the combustion method for halogens and sulfur, the electrolytic determination of copper, molecular weight determination by the ebullioscopic method, and the determination of methoxyl, ethoxyl, and methylimino groups. During this period, about 10,000 exact weighings were made. Pregl's first public announcement of these methods was made before the German Chemical Society in Berlin on February 27, 1911, with demonstration of his technic. The results were first published in Abderhalden's Handbuch der Biochemischen Arbeitsmethoden in 1912.

In 1916 the first edition of Pregl's book was published. By this time the micromuffle for the microdetermination of metallic residues had been worked out, also the carboxyl group determination, and the technic developed for the analysis of low-boiling liquids for carbon and hydrogen, and the gravimetric determination of arsenic. At the time of publication of the second edition in 1922 new determinations included the volumetric determination of arsenic, the determination of mercury in organic compounds, the determination of the acetyl group, and the ebullioscopic determination of the molecular weights of liquids. Up to the time of the publication of the third edition in 1930 many industrial laboratories of Europe had adopted quantitative organic microanalytical methods, which had been spread to all countries of the world by over three hundred of Pregl's students. Pregl received the Nobel Prize in Chemistry in 1923 for his development of these methods.

Microchemical analysis had such widespread acceptance, particularly in Europe, that many new methods were worked out, or new applications discovered, and some suitable medium for publication had to be found. In 1922 Emil Haim and Co., Leipzig and Vienna, undertook the publication of *Mikrochemie*, which was devoted solely to papers on microchemical topics and edited by such well-known microchemists as Pregl, Emich, Lieb, Strebinger, and Feigl.

The Microchemical Balance

The success of all the above methods was dependent upon the development of a balance which was capable of weighing microsamples with at least the same precision as the ordinary analytical balance is capable of weighing macrosamples. The main contributor to this development was W. H. F. Kuhlmann of Hamburg, Germany. His first balances had a capacity of 20 grams and weighed accurately to 0.01 to 0.02 mg. At the suggestion of Pregl, and with advice offered by him, Kuhlmann attempted to increase the sensitivity one more decimal place by improving the grinding of the knife edges and using the utmost care in having the agate bearings

not only all in one plane but also absolutely plane parallel. In 1911 Kuhlmann assembled the first balance having a sensitivity of 0.001 mg., the last two decimal places being read on the fixed scale in front of the pointer. Thus it became possible for an experienced microanalyst to weigh a 2-mg. sample with approximately the same precision (1 part in 2000) as one could formerly weigh a 0.2-gram sample on an ordinary analytical balance; by using 3 to 5 mg. of substance the error is less than that made when weighing a 0.2-gram sample on an analytical balance. Despite its high sensitivity, this balance has proved very durable and there are cases where it has been in daily use in industrial laboratories for six years, with 36,000 estimated weighings being made before any adjustments, other than periodic cleaning, were necessary. A rather large number of firms now make microchemical balances but, besides the Kuhlmann balance, the only other balance recommended by Pregl is that of Starke and Kammerer of Vienna. This balance has two interchangeable sensitivities (0.01 and 0.001 mg.), so that it is unnecessary to arrest the balance and move the rider so often, which makes for less wear on the knife edges, agate bearings, and other moving parts. Other manufacturers of microchemical balances include: Sartorius, Göttingen; Bunge, Hamburg; Stückrath, Friedenau b. Berlin; Nemetz, Vienna; Rueprecht, Vienna; Ainsworth, Denver, Colo.; and Becker, New York, N. Y.

Microchemical Apparatus

The necessary apparatus was developed by Pregl during the progress of each investigation; in general, the glass apparatus was made originally by Pregl himself and later by the firm of Paul Haack in Vienna, under Pregl's supervision; the iron ware and metal apparatus was made by the university mechanic. The refined chemicals were at first purified by Pregl, but later E. Merck and Company furnished them according to his specifications.

At present this apparatus can be purchased from Paul Haack in Vienna. Haack has appointed an authorized American agent, Microchemical Service, Douglaston, N. Y., from whom these apparatus and reagents can be procured, as well as the Kuhlmann and Starke-Kammerer microchemical balances.

Microchemical Equipment of Coal Research Laboratory

The installation of a microchemical division in the Coal Research Laboratory of the Carnegie Institute of Technology seemed particularly important, since a large part of its investigations were to be on a laboratory scale where relatively small amounts of material would be available. Because of the complexity of the coal molecule, one is certain to obtain a complex mixture of products from any reaction conducted upon it, and if a relatively small amount of starting material is used the separation, purification, and identification of the products is obviously a problem best solved by the application of microchemical technic. Most completed, successful investigations on coal which deal with the isolation of products have started with extremely large amounts of material; others have not been successfully completed because "an insufficient amount of material was at hand to permit further identification." The quotation just cited is a constantly recurring one, especially in the older literature and before the development of microchemical technic.

The Coal Research Laboratory purchased a complete set of apparatus for all procedures involving the following microdeterminations:

Carbon-hydrogen
Nitrogen (Dumas)
Nitrogen (Kjeldahl)
Halogens and sulfur (by combustion)
Halogens and sulfur (by Carius method)
Molecular weight (by elevation of the boiling point)
Molecular weight (Rast method)
Methoxyl and ethoxyl groups
Methylimino group
Phosphorus in organic compounds
Arsenic in organic compounds
Acetyl group
Carboxyl group
Residue or ash

Subsidiary apparatus includes apparatus for purification of small amounts of material, Kuhlmann microchemical balance, and Starke-Kammerer microchemical balance. The laboratory is thus equipped to do routine or special elementary analyses on practically any organic product which may be obtained in the course of the work. This apparatus was all purchased directly from the foreign manufacturers or distributors, the total cost, including duty, consular fees, transportation, packing, etc., being: Apparatus (Paul Haack), $400; Kuhlmann balance, $185; Starke-Kammerer balance, $275; a total of $860.

Sampling for Microchemical Analysis

This subject has been thoroughly discussed by Benedetti-Pichler (*2*). A criticism often directed against microchemical methods of analysis is that it is impossible to get a true representative of the whole sample in the very small amount of material (2 to 3 mg.) necessary for a microanalysis. In macro- or microanalysis it would be impossible to get a representative sample if the particle size of the mixture was so large that only a few grains were taken for weighing. In each case one is forced to pulverize the sample if one cannot, or does not wish to, increase considerably the size of the sample for analysis. If it is possible to take from a carload, containing 15 short tons of large-sized material, 100 kg. (0.75 per cent) and then, after thoroughly grinding and mixing this amount to take a representative sample of 10 grams (0.01 per cent of 100 kg.) or less, it is just as possible to get a representative sample weighing 1 mg. (0.1 to 0.01 per cent) from 1 gram or 10 grams of the original substance which had first been finely pulverized.

The following factors are of importance in the preparation of representative samples for microanalysis:

The sample should be capable of being very finely pulverized, for, in the weight of an individual particle, the third power of the diameter of the particle appears in the calculation. Generally, metals and alloys cannot be pulverized sufficiently fine to yield a representative sample weighing but 5 mg. In this case the sample may be made homogeneous by fusing it so that each filing from the fusion product is a representative sample in itself. One must insure that in the cooling of the melt selective crystallization or segregation does not occur.

The density of the material only linearly influences the weight of an individual particle. One must guard against a settling out of various constituents of different densities during the mixing and grinding, particularly if the densities differ greatly.

Very different hardness of the constituents of the mixture may cause the hard particles to become imbedded in the softer material during grinding and to escape being pulverized.

The procedure of fine grinding was tested experimentally on synthetic mixtures involving two and three constituents: (1) potassium sulfate and sodium chloride; (2) sulfonal and potassium sulfate; (3) sulfonal, azobenzene, and potassium sulfate. These mixtures were analyzed, respectively, for chlorine; carbon, hydrogen, and ash; and carbon, hydrogen, nitrogen, and ash. Completely satisfactory results were obtained, and it was concluded that this method is applicable to all mixtures of a salt-like character which can be finely pulverized. Samples weighing less than 3 mg. could be used for the analysis, while for residue determinations a fraction of a milligram sufficed.

Next, bituminous coal was analyzed. Microdeterminations of moisture are not possible where, as a result of the official sampling of several carloads of coal, the chemist gets a number of samples of various particle size. This determination should show the moisture content of the mine run coal and very little mixing and pulverizing should be done.

For the determination of all the constituents, the chemist receives a bottle containing the more or less finely pulverized coal representing the final result of the sampling process. The moisture content no longer represents the mine condition, and there is no harm in pulverizing the sample as finely as possible and carrying out analyses on the pulverized sample. Such microdeterminations have previously been made on coal in Pregl's laboratory, in Lipp's commercial laboratory in Graz, and by Strebinger and Radlberger (*23*).

Fifty grams of German bituminous coal, in fairly large pieces, were crudely ground in a mortar (sample A). Five grams of sample A were pulverized for 5 minutes (sample B). A carbon-hydrogen determination on sample B showed that the mixing was not yet sufficient to yield concordant results; according to Müller and Willenberg (*19*), one can recognize a nonhomogeneous sample by the fact that the analytical results may vary by as much as 1 per cent. Consequently 1 gram of sample B was pulverized for 5 minutes in an agate mortar (sample C). The analytical data follow:

Table I. German Bituminous Coal

Macrodetermination of Moisture and Ash, Sample A

Weight of sample = 4.7960 grams
Loss in weight = 0.0400 gram after drying 2 hours at 110° C. = 0.83% H_2O
Weight of ash = 0.0864 gram = 1.81% ash

Macrodetermination of Ash, Sample B

Weight of sample = 1.0000 gram
Weight of ash = 0.0180 gram = 1.80% ash

Microdetermination of Carbon-Hydrogen and Ash, Sample B

Weight of sample	Carbon	Hydrogen	Ash
Mg.	%	%	%
4.562	84.62	5.35	2.35
4.971	84.55	5.17	1.85
3.720	85.61	4.96	1.61
Mean	84.93	5.16	1.94

Microdetermination of Carbon-Hydrogen and Ash, Sample C

Weight of sample	Carbon	Hydrogen	Ash
Mg.	%	%	%
4.392	84.51	4.71	2.32
3.455	84.35	5.21	2.08
4.679	84.48	4.42	2.14
3.458	84.49	5.18	2.11
4.736	84.50	5.39	2.18
4.212	84.65	5.21	1.90
Mean	84.50	5.02	2.12

Volatile Sulfur and Ash Determination, Sample C

(Combustion method)

Weight of sample	Sulfur	Ash
Mg.	%	%
6.724	2.65	1.99
5.483	2.63	2.04
5.097	2.56	1.97
Mean	2.61	2.00

Moisture Determination, Sample C

(Pregl drying block)

Temp.	Weight of sample	Decrease in weight after minutes: 20	40	45	60	H_2O
° *C.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	*Mg.*	%
107	5.372	0.039	0.045	...	0.045	0.84
107	4.925	0.039	0.043	...	0.043	0.87
102	3.582	...	...	0.028	...	0.78
					Mean	0.83

Moisture Determination, Sample C

(Pregl microdesiccator)

Weight of sample = 5.014 mg.
Temperature = 107° C.
Decrease in weight = 0.018 mg. after 5 minutes
Decrease in weight = 0.030 mg. after 20 minutes
Decrease in weight = 0.030 mg. after 45 minutes = 0.60% H_2O

Moisture Determination, Sample C, with Uninterrupted Drying

(Pregl microdesiccator, temp. 107° C.)

Weight of sample	Decrease in weight	H_2O
Mg.	*Mg.*	%
7.094	0.041 after 20 min.	0.58
4.010	0.022 after 25 min.	0.55
3.320	0.013 after 45 min.	0.39

The values obtained for carbon on sample C show the complete homogeneity of the sample that had been obtained for the microanalyses.

The values obtained in the microdeterminations of ash are somewhat discordant because of spattering. Since spattering is caused by decrepitation of the coal due to its moisture content, this effect is diminished by fine grinding and losses in the ash determination are smaller in microdeterminations than in macro- because the combustion proceeds much more slowly. The mean value obtained from the microanalyses is therefore probably more accurate than that yielded by the macromethod.

The hydrogen values vary considerably because of the hygroscopicity of the coal. In the above experiments the coal was always weighed in an open boat. If somewhat more time was used and Pregl's stoppered weighing tube employed, a greater constancy of hydrogen values would undoubtedly be obtained. In practice one would combine the moisture determination with the carbon-hydrogen determination and thus burn the dried coal. Reabsorption of moisture would be excluded by using microanalytical technic, for the dried sample would be put directly into the glass-stoppered weighing tube while still hot, and exposed to the outside atmosphere for only a few seconds while being transferred to the combustion tube.

Using Pregl's microdesiccator for the determination of moisture and drying at 107° C. for 20 minutes in a partial vacuum gives results which are about 0.2 per cent low. That this is due to oxidation of the sample by the small amount of air which passes over it is confirmed by the fact that uninterrupted drying in this apparatus for 45 minutes gives results about 0.4 per cent low. More rapid and accurate results would be obtained by passing an inert gas, such as carbon dioxide or nitrogen, over the sample in place of air.

For the sake of speed and convenience the determination of sulfur could be made acidimetrically, rather than gravimetrically, by titrating the solution obtained from the combustion. If one used Pregl's procedure the results would not be absolutely precise, owing to the presence of nitrogen (and possibly halogens) in the coal, but might be sufficiently precise for certain cases. By using Friedrich's method (*11*) precise results can be obtained titrimetrically despite the presence of these elements.

The determination of carbon, hydrogen, and ash can be made in 45 minutes with a little practice. No special precautions need be taken in the combustion of coal. The small sample is rapidly gasified and then almost nothing but carbon remains and one can proceed with the movable burner directly under the boat, because in the reaction $C + O_2 = CO_2$ there is no volume change in the gas phase and no danger of a backing-up of the gas with subsequent cessation or back-flow of the bubble-counter.

The determination of sulfur, volumetrically, coupled with an ash determination requires about 2 hours, of which 1.25 hours represents actual working time. Determination of moisture, using the drying block, requires 45 minutes but only 25 minutes if one uses the microdesiccator. Thus a complete ultimate analysis of coal, plus moisture and ash determinations, requires but 3 or 4 hours. The time per analysis is further shortened if a series of analyses is made.

Sampling Industrial Materials for Microanalysis

Lucas and Grassner (*16*) state that the results of analysis on 10-mg. coal samples are the same as those obtained with twenty times this amount in a macroanalysis and that no special sampling is required for microanalytical determinations. The final 125-gram sample, which is taken in a definite way, is finely ground and sieved through a metal sieve having 1600 meshes per square centimeter (about 100 meshes per inch), so that a dust-fine, homogeneous powder is obtained. Table II illustrates the excellent agreement obtained.

Table II. Comparative Determinations

Coal	Macrosample (Approx. 200 mg.) Carbon	Hydrogen	Microsample (Approx. 10 mg.) Carbon	Hydrogen
	%	%	%	%
Run of mine	77.94	4.28	77.82	4.17
Nut	82.59	4.67	82.49	4.64
Anthracite	81.20	4.30	81.33	4.26
Mid-German brown	59.44	6.28	59.26	6.29
Humus	50.18	5.22	50.20	5.41
Lignite	41.90	5.81	41.86	5.85

Strebinger and Radlberger (*23*) carried out microanalyses on coal as a test of the possibility of getting a homogeneous

representative sample from a nonhomogeneous material. Even in macroanalysis the sample taken for analysis is usually representative of many tons and is made homogeneous by pulverizing. Any inorganic impurities which are present and not uniformly distributed will cause large errors whether 3 mg. or 0.3 gram are weighed. One must thus proceed in the same way for preparing samples for either macro- or microanalyses and the sample must be thoroughly pulverized in an agate mortar. Comparative results on different types of coal are given below.

Table III. Comparative Determinations

Coal	Macrosample				Microsample			
	Carbon	Hydrogen	Ash	H_2O	Carbon	Hydrogen	Ash	H_2O
	%	%	%	%	%	%	%	%
Brown	41.01	3.50	6.38	25.80	41.33	3.58	6.21	25.92
Russian I	52.26	6.75	13.39	16.13	52.40	6.77	13.50	16.27
Russian II	67.50	4.81	3.97	11.81	67.76	4.67	4.02	11.97

The results agree satisfactorily and because of the great advantages of the micromethod the authors decide in favor of it.

Strebinger and Radlberger also made comparative micro- and macroanalyses on two other industrial materials, nickel in a nickel steel and sulfur in pyrites; satisfactory agreement was obtained by the two methods. In the macroanalysis of the steel, because of its low nickel content, 20 grams were used, whereas 10 mg. sufficed for the microanalysis.

For a theoretical discussion of sampling for microanalysis, see Mika (*18*) and Baule and Benedetti-Pichler (*1*).

Advantages of Microanalytical Methods to Industry

Economy of Materials. Goubau (*14*) points out that one of the principal advantages of microchemical methods is that they use very small amounts of material. This advantage, of little importance in ordinary industrial analysis, may be very important in industrial laboratories dealing with biological, mineralogical, or organic products. Very often in a research one obtains a very small amount of a substance which is not sufficient for analysis using macromethods. Micromethods may be the deciding factor in the success of the research and, for this reason alone, deserve a place in all scientific, research, and industrial laboratories. Von Braun (*5*) stresses the importance of the saving of valuable materials, particularly at the present time when organic chemistry is working farther into the field of biochemical processes where the investigator often has a minimum amount of exceedingly valuable substance isolated from plant or animal bodies. Thus, a series of valuable investigations, such as those of Wieland on toad poisons, or Levene on nucleic acids, or work dealing with enzymes, hormones, vitamins, etc., would probably have not been possible without the aid of microchemical methods of analysis.

An illustration of the economy of microchemical analysis is cited by Cornwell (*9*): A certain company required an analysis on a substance worth $5000 per gram, only 0.3 gram being available. A macrodetermination of carbon and hydrogen would completely destroy 0.2 gram having a value of $1000. A microdetermination would use but 2 mg. worth but $10. Flaschenträger (*10*) estimated that he and his co-workers, in the period from 1920 to 1926, made 3000 carbon-hydrogen, 1000 nitrogen, 200 halogen, sulfur, and methoxyl, and 500 residue microdeterminations. Cornwell, assuming a 0.2-gram sample for each macrodetermination, calculates that 940 grams of material would have been burned in the making of these 4700 analyses by macromethods, whereas, assuming an average of 2-mg. samples for each microanalysis, only 9.4 grams were destroyed. If smaller samples are used, other materials—gas or electricity, tap and distilled water, reagents, etc.—will be reduced proportionately and there is also a considerable saving of space.

Microchemical methods also permit working safely with extremely explosive substances. Thus, Riesenfeld and Schwab (*21*) were able to make a complete study of very pure ozone, using but a few milligrams. Working with large amounts would have been very dangerous.

The economy of reagents is very great, usually requiring from one-tenth to one-hundredth the amount necessary for a macrodetermination.

Using microtechnic and a Schwarz-Bergkampf filtering beaker, Benedetti-Pichler (*3*) made a single nickel determination in 1 hour, of which but 0.5 hour was actual working time. Less time per analysis would be necessary if a series was made. Only 5 mg. of dimethylglyoxime and 0.5 cc. of absolute alcohol were necessary, which is approximately one-hundredth that required for a macroanalysis. The precision of this method is attested by the fact that Schwarz-Bergkampf, using 1 to 1.5 mg. of nickel ammonium sulfate, got the following results in five analyses: 14.72, 14.85, 15.07, 14.78, and 14.63 per cent of nickel; mean, 14.81; theory, 14.86 per cent.

Because of the economy of reagents it is permissible to use precious substances such as platinum or palladium salts, smaller apparatus is used, and the expense due to breakage is less. This also permits the more general use of platinum apparatus, so that errors due to inclusion of soluble portions of glass, etc., in precipitates are avoided, making the determinations more precise.

To illustrate comparative costs of apparatus for micro- and macrowork, Pichler discusses Pregl's electrolytic copper determination. For the microdetermination the electrolysis is carried out in a small test tube. The platinum wire gauze cathode and platinum wire anode, if of heavy construction, weigh but 2 grams, while the macroelectrodes total 16 to 18 grams. Electrolyzing 4 to 5 cc. of a sulfuric acid solution requires 10 to 20 minutes for quantitative deposition. With one stand and two pairs of electrodes (4 grams of platinum), one analyst could make 30 microdeterminations of copper in 10 hours. To make the same number of macrodeterminations in the same time would require at least six pairs of electrodes (100 to 110 grams of platinum).

Economy of Time. This is one of the most important advantages of micromethods. The determination of carbon, hydrogen, and nitrogen by macromethods represents nearly a day's work, whereas the same determinations can be made microanalytically in 1.5 to 2 hours.

Flaschenträger (*10*) states that the normal day's work for an experienced microanalyst is eight carbon-hydrogen and four nitrogen determinations. Meixner and Kröcker (*17*) state that in their laboratory a carbon-hydrogen determination requires 50 to 55 minutes (which confirms Pregl's estimate), but that one analyst cannot make eight determinations in an 8.5-hour day if he has to pulverize and dry the samples to constant weight before each analysis.

The micro-Kjeldahl method requires about 5 to 15 minutes for complete digestion and only 4 minutes for distillation of the ammonia; a single determination can be made in less than a half-hour, the time factor becoming more favorable if a series of analyses is conducted at one time. Bermann (*4*) points out the advantage of this micromethod over other methods, under actual technical conditions. He used barley, yeast, and molasses, all of which differ considerably and show the practicability of the method. Here also, the contention that a few milligrams of substance cannot be a representative sample of a large amount of material was disproved. Comparative results obtained from the two methods (macro and micro) differed by but 0.03 to 0.04 per cent.

From the practical standpoint Bermann claims that one can make eight microdeterminations of nitrogen in the same time, with the same precision and with only one-tenth the reagents necessary to make one macrodetermination. From the scientific standpoint the microdetermination of nitrogen is very important to the fermentation industry because it opens up possibilities which are not attainable by macromethods—for example, a study of the morphological elements of the barley seed, the change in the nitrogen content during germination, etc., which can be studied with a single granule. Technically, the method is important because of its great speed which makes it possible to change the mash ratios immediately and while the fermentation proceeds.

The micro-Dumas method for nitrogen, using a 1- to 4-mg. sample, can be made in 1 to 1.25 hours, including weighings, and is more accurate than the macromethod. In the latter method correct results were due to fortuitous compensation of errors, whereas the micromethod is rational. The refinements, discovered during the establishment of the method, include an exact definition of combustion velocity as measured by the number of gas bubbles per second, improvement in the preparation of air-free carbon dioxide, and finally placing the reduced copper section in the middle of the tube rather than at the end. Pregl showed that glowing copper, especially if impure, reduced carbon dioxide to carbon monoxide, causing the nitrogen values to be too high. By having the reduced copper layer followed by copper oxide at the proper temperature this error was removed.

For the determination of halogens and sulfur the microcombustion method is advantageous if one wishes to get a single result quickly, requiring about 1.5 to 2 hours, of which about one-half is actual working time. If the volumetric determination is substituted for the gravimetric there is a still greater saving of time and the tedious filtration of the small amounts of precipitate is avoided as well as the elimination of two weighings of the filter tube, microcrucible, or filter stick and crucible. For a series of determinations of halogens or sulfur the micro-Carius method is probably best, since several tubes may be placed in the bomb furnace at once. An average of about 4 hours' heating is necessary for complete decomposition, compared to 8 to 24 hours for macrosamples; the micromethod has the advantage also that the small tubes can be rapidly brought to 275° to 300° C. in the furnace and rapidly cooled again to room temperature, whereas this occupies considerable time in the macro-Carius method. The danger of explosion of these small pressure tubes with resulting injury to the analyst is nil.

The other determinations, such as microcarboxyl, methoxyl, ethoxyl, acetyl, etc., are similarly rapid when compared with the corresponding macromethods.

The advantage of rapidity coupled with precision is especially great in an industrial laboratory where a large series of analyses is made. The rapidity in getting results enables a process operator to know, during the progress of his process, just what is going on and, if necessary, to make rapid corrections as suggested by the analysis.

Experiences of Various Laboratories

Meixner and Kröcker (*17*) state that the I. G. plant at Höchst a/M chose microanalytical methods because of their certainty, precision, and economy of materials. Grassner (*15*) points out that microchemical methods first gradually extended from university laboratories to medico-chemical laboratories of the pharmaceutical industries where they were applied in the scientific investigation of medicinals. Later microanalysis went into the chemical-technical research laboratories of industry where it was at first skeptically received. However, it proved of value to industry and is used in an increasing circle of chemical-technical investigations. These methods are used in industries where there is no shortage of material, because of the economy of space, energy, and time and because of their increased precision. They are also most useful in searching for "traces" in industrial products. In the I. G. chemical-technical research laboratory quantitative organic microanalysis was introduced in 1922 and is used almost exclusively.

Microchemistry as an industrial economy has been discussed by Gesell and Dittmar (*13*), who state that one of the chief factors in the cost of chemicals is the cost of control and a reduction of this item by means of the practical application of microchemical methods seems promising. Three serious difficulties are: The assumption that specialized workers are necessary and that the average analyst is not capable of adapting himself to methods using smaller quantities of material where the factor of error would be greater; the difficulty of sampling for microchemical methods; and the difficulty of obtaining equipment not too complicated nor too delicate for practical purposes. Experience has shown that these are easily overcome. The average, capable, intelligent analyst can easily adapt himself to microtechnic; representative samples can be obtained if proper precautions are taken; and, finally, the equipment is easily obtainable and no more complicated or fragile than ordinary apparatus. Gesell and Dittmar present data on parallel macro- and semi-microanalyses on the same materials involving ash, Kjeldahl, and residue determinations, and conclude that microchemical methods would effect marked economy in the cost of analytical control. They estimate that in large concerns, where the laboratory costs run between $20,000 and $100,000 per year, a saving of 50 to 60 per cent could be effected.

Goubau (*14*) points out certain disadvantages of microchemical methods, which necessitate meticulous, painstaking technic, not always applicable in an ordinary laboratory. However, Pichler states that microchemical methods require no special ability on the part of the analyst. It is true that the microchemical balance is a very sensitive instrument which must be handled delicately to yield good results and have a long life, but the technic of weighing with it and of cleaning it at definite intervals is very easily learned.

Gault and Nicloux (*12*) discuss the analysis of some bituminous minerals submitted to the petroleum laboratory of the University of Strasbourg. These samples contained only 11 to 30 per cent of carbon and 1.7 to 3.0 per cent of hydrogen. To get satisfactory macroresults the combustion had to be conducted for 4 to 5 hours; for satisfactory microresults, because of the low percentage of hydrogen present, samples weighing 15 to 20 mg. were used, the combustion requiring but 50 to 60 minutes. The following data show comparative results on the same samples:

Table IV. Comparative Results on Same Samples

Sample	Macroanalysis Carbon	Macroanalysis Hydrogen	Microanalysis Carbon	Microanalysis Hydrogen
	%	%	%	%
1	24.60	3.68	25.15	3.65
2	11.02	1.45	11.27	1.53
3	21.80	2.29	22.27	2.38
4	23.63	2.65	23.70	2.73
5	14.65	1.82	14.57	1.85
6	29.94	3.18	29.90	3.21
7	16.50	1.66	16.98	1.83

The authors conclude that micromethods are not only more simple and rapid but are more exact and more general than macromethods. Pregl's methods can also be extended to the analysis of fuels in general.

In a recent article Clark (*7*) points out that Pregl's micromethods are as accurate as standard methods and, aside from the economy of material, they require less time, reagents, and space for the execution of the work and are preferred even when a plentiful supply of material to be analyzed is available. Adoption of micromethods is not confined to research laboratories but routine and control laboratories are also using these methods with an appreciable saving in financial upkeep.

However, the change from macro- to micromethods in routine and control work has not been as general as appears warranted. To overcome the arguments often directed against Pregl's methods—namely, that for routine and control work the technic of this system demands too high a degree of analytical skill, the work tends to become tedious, and a special laboratory must be used—Clark recommends a semimicromethod using samples ranging from 5 to 25 mg. and claims that requirements as to details, laboratory conditions, balances, etc., are not nearly so exacting as those imposed by the microsystem but possess the other advantages as to economy of time, space, and reagents.

In numerous cases cited in the literature increasing the size of the sample is recommended to make the results surer and the technic simpler. Probably the foremost advocate of the semi-micromethod is J. Dubsky. However, Pregl has

stated (*20*) that the advantages claimed for the increase in the size of the sample are questionable. Schöller has also pointed out (*22*) that beginners often attempt to make the work easier by increasing the size of the sample. However, with careful weighing, errors in technic do not occur during weighing but rather are due to incomplete combustion, and the probability of error is considerably increased by enlarging the size of the sample. One of the most important advantages of the micromethod is immediately lost by increasing the size of the sample used in the analysis.

No special skill is required to master the technic of the micromethods as devised by Pregl. There is also probably little to choose between the tediousness of the micromethod compared to the semi-micro- or the macromethod; but since the micromethod is more rapid than either of the other two methods the long extended waiting periods for reactions or processes to complete themselves are very much shortened. For ordinary routine analyses no special room is necessary for use as a microanalytical laboratory. Some care must be used in the selection of a proper place for the microbalance as is also advisable in case of a high-grade analytical balance. The room in which analyses are carried out should be as free as possible from dust, corrosive fumes, and organic vapors, but these same conditions should apply, in general, to an ordinary analytical laboratory.

It is not to be implied that micromethods must, of necessity, ultimately completely replace macromethods; the two methods should be used together. Working with small quantities increases our knowledge of the errors in macroprocesses and often points the way to new methods. Clarke (*8*) states that the microanalytical group, in addition to its obvious function of performing analyses on samples too small for macrochemical attack, is also charged with the task of subjecting to critical scrutiny the methods employed in the general laboratory, with a view towards incorporating into these methods any points of technic derived from microanalysis that will reduce the time required for their performance or increase their precision.

The substitution of micro- for macromethods will occur only where it is found that the former are better suited to the particular needs and conditions of a given laboratory. Likewise, microchemistry need not be considered as a special field but rather as a supplement to macrochemistry. It is impossible to deny the value of micromethods to both the scientific and industrial laboratory, for microanalysis today is one of the indispensable tools of research and has already rendered much valuable service in many branches of science. Industry would be making a mistake if it too did not take advantage of the aid microchemical methods can offer in the solution of its problems.

Experience of Coal Research Laboratory

Experience in the Coal Research Laboratory confirms the statements concerning the precision, speed, and economy of microchemical methods.

The sample of bituminous coal which all units of the laboratory are investigating has been analyzed by Silbert, using samples of various particle size. After pulverizing thoroughly in an agate mortar these samples were analyzed and the following data (Table V) show that there is no difficulty in getting a representative sample for microanalysis, for results satisfactorily check those reported by the Bureau of Mines for the same coal and are, of course, made with much greater speed and economy of reagents and materials.

The considerable difference in the values obtained for ash and moisture are not unexpected and are accounted for by the fact that the samples were prepared in another department by grinding in a rod mill in a current of natural gas. Such treatment would tend to raise the ash content of the sample and diminish the moisture content. On a moisture- and ash-free basis, however, the checks are satisfactory. Table VI shows the excellent checks which are obtainable on the same sample (4 to 8 mesh) in the determination of carbon-hydrogen, nitrogen, sulfur, and ash, which proves the sample to be homogeneous.

Table V. Analysis of Coal Sample from Edenborn Mine

Sample	Moisture	Ash	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
	%	%	%	%	%	%	%
Bureau of Mines analysis							
As received	1.9	7.5	77.4	5.2	1.6	7.3	1.0
Moisture-ash free	..	..	85.5	5.5	1.8	6.1	1.1
Coal Research Laboratory microanalysis							
4–8 Mesh[a]							
As received	1.19	8.30	77.27	5.25	1.60	6.59	0.99
Moisture-ash free	..	..	85.38	5.57	1.77	6.19	1.09
16–20 Mesh[b]							
As received	1.01	7.48	78.26	5.25	1.63	6.40	0.98
Moisture-ash free	..	..	85.52	5.55	1.78	6.07	1.08
60–80 Mesh[b]							
As received	1.12	8.30	77.39	5.32	1.61	6.41	0.97
Moisture-ash free	..	..	85.44	5.67	1.78	6.04	1.07

[a] Results are mean of 5 determinations.
[b] Results are mean of 3 determinations.

Table VI. Check Determinations

Sample	Moisture	Ash	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
	%	%	%	%	%	%	%
As received	1.19	8.31	77.19	5.28	1.55	5.48	1.00
Moisture-ash free	..	..	85.32	5.61	1.71	6.26	1.10
As received	1.19	8.31	77.28	5.24	1.58	..	..
Moisture-ash free	..	..	85.39	5.57	1.74	..	..
As received	1.19	8.32	77.27	5.21	1.61	5.40	0.99
Moisture-ash free	..	..	85.40	5.53	1.79	6.19	1.09
As received	1.19	8.29	77.32	5.30	1.64	..	..
Moisture-ash free	..	..	85.41	5.63	1.81	..	..
As received	1.19	8.29	77.30	5.21	1.61	5.42	0.98
Moisture-ash free	..	..	85.39	5.53	1.78	6.22	1.08

Analyses have also been made on a wide variety of products isolated by the various units of the laboratory, and on gas gums furnished by the research laboratory of the Koppers Company. The formation of these gums at small orifices (pilot burner tips) was a great annoyance, as it led to the extinction of the pilot light with the resulting danger of asphyxiation or explosion. The accumulation of even a few milligrams of these gums requires several weeks and the amount of time necessary to collect 0.2 gram, the amount needed for an ordinary macroanalysis, can be readily calculated. This represents a case where there is not only a saving in the time for the actual conduct of the analysis but a tremendous saving in time in the collection of a sample of suitable size for analysis.

Conclusion

In general, American chemists have been slow to realize the advantages to be gained by the use of microanalytical methods, not only in industrial laboratories but also in university and scientific laboratories. European laboratories adopted micromethods shortly after the first work of Pregl appeared; practically every university and technical institute has its microanalytical laboratory, and European industrial laboratories have also widely adopted these methods. Some progress has been made in this direction in this country, however, as judged by American scientific and industrial journals which are reporting an increasing number of microanalyses.

The advantages of microchemical methods are so numerous and so obvious that their general adoption in American laboratories is certain to occur. Those laboratories which postpone their adoption are losing an opportunity to save time, energy, and money. Now, when economy is almost a world religion, would seem to be an ideal time in which to introduce these methods generally into American laboratories.

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Apparatus for Microanalysis of Gas

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The need for a device for microanalysis of a large number of gas samples led to the design of the apparatus herein described. It is intended to be easily constructed, convenient, and simple to operate, and to eliminate much of the time-consuming tediousness so often present in both micro- and macromethods. The method is identical in principle with that of Blacet and Leighton (*1*) and the same accuracy is attained. It differs in the mechanical arrangement of the essential parts and in the mode of operation. Two sets are in use in the authors' laboratories and have been found satisfactory.

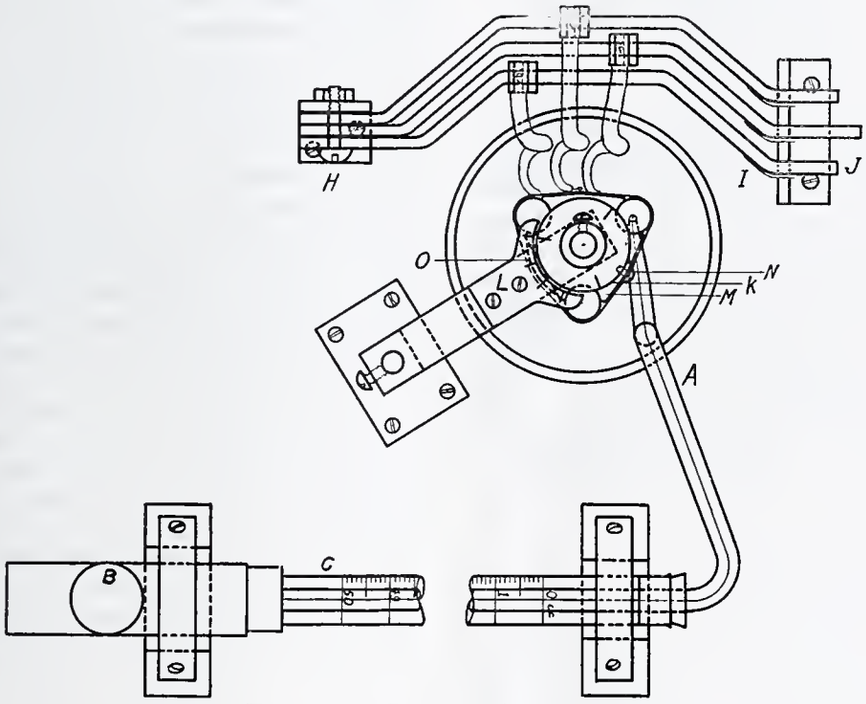

Figure 1. Plan of Apparatus

The advantages of the arrangement lie in the use of a horizontal capillary buret instead of the vertical type used by Reeve (*5*), Christianson (*3*, *4*), and Blacet and Leighton (*1*), and in the use of separate lever mechanisms for convenient introduction of the various solid reagents into the gas. The horizontal buret has several distinct advantages. It permits the tip of the buret to be quickly and easily raised into the gas containers with the fingers. It eliminates the tendency to leak because there is no pressure on the rubber pouch due to a column of mercury. Readings may be made in any section of the buret, as the pressure is not changed by the position of the gas. A trap is not needed to protect the buret from bits of sealing wax, gas bubbles, etc. These impurities float to the top, whereas the outlet into the buret is on the side. The customary trap or enlargement at the end of the buret to guard against loss of gas into the rubber pouch will not work in a horizontal position. A piece of large capillary tubing may be inserted instead, reserving the last fourth of the buret for this protection.

Apparatus

Figure 1 is the plan of the apparatus drawn to scale. The parts are mounted on a moderately heavy board, such as 1.25 × 12 inches × 2.5 feet, which stands on rubber-headed tacks for legs to prevent sliding on the table.

The solid reagents, or beads, must be kept submerged in mercury when not in use and must not touch the walls or bottom of the inverted gas container while being used (*5*). To move the beads accurately and quickly they and their accompanying glass supports are attached to levers. This gives each bead a path of motion along an arc which is practically a straight line. If the level of the center is that of the midpoint of the arc, the lateral motion will be a minimum. For 1 inch (2.5 cm.) of vertical motion the lateral motion d is given as a function of the radius r by the expression

$$d = r - \sqrt{r^2 - 0.25}$$

For a radius of 2 inches (5 cm.) the lateral deviation is about 0.0625 inch (0.16 cm.), and any greater radius would allow only a negligible lateral motion.

Figure 1 shows the top view of the levers each carrying a bead and glass support. The glass supports are curved so that their proximity to each other does not interfere with their motion about the center at H. A thin sheet of brass is soldered to the lever at I to give friction. Obviously the bead must be placed in the gas with some precision: it must be well up into the gas space but must not touch the top of the tube. If the levers had been made straight, any rotary motion about the line HJ, as by twisting at J while adjusting the position of the bead, would make this adjustment more difficult and inaccurate in the event that the bearing at H was not well fitted. To reduce this effect the levers are bent as shown in Figure 1 to bring the bead nearer in line with the movable end J and the pivot H.

The tip of the buret is raised up into the gas containers by rotating the whole buret about its axis. This motion is con-

veniently and accurately produced by movement with the fingers at A, better shown in Figure 2. The distance from the center of rotation to the tip is about 4 inches (10 cm.), so the lateral motion here is only about 0.03 inch (0.07 cm.)

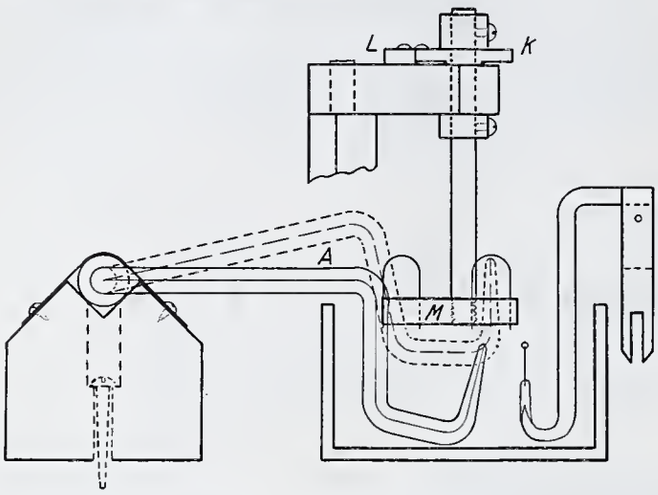

Figure 2. Right End View

The diameter of the buret is determined by balancing two opposing factors. If a gas sample is large, too much time is required for reaction and, if small, too fine a capillary must be used for the buret with consequent excessive sticking of the mercury. Probably the optimum dimensions would require a capillary 0.5 to 0.7 mm. in diameter. Capillary tubes are generally far from uniform in cross section and must be carefully calibrated. The authors used Christianson's method (*3*). The graduated cylinder of a 50-cc. buret serves very well for the glass protecting tube C, Figure 1. It furnishes easily readable uniform graduations as well as an air jacket for thermal protection. A large water jacket may be used but it is generally unnecessary for analyses of short duration.

Any of the various devices described in the literature for moving the mercury thread should work very well in this apparatus. The authors controlled the mercury thread by means of a rubber tube inclosed in a metal case similar to the pouch and barrel of a fountain pen. The thumbscrew B, Figure 1, is used to compress the pouch. The metal case is rigidly sealed to the protecting tube C with sealing wax.

Again looking at Figure 1, three marks or graduations may be seen on the knob or dial indicated by K and four marks corresponding to the position for the buret and to positions for the three beads may be seen on the plate L fitting up to this dial. These are for setting the gas container assembly in proper position for use of the buret or a reagent as the case may be. The gas container support M is shown as a triangular block of iron 0.25 inch (0.62 cm.) thick with circular grooves cut at the corners for accommodation of the glass gas containers. The latter are held in place by a very thin iron band whose ends are both held by the screw at N. This iron strap is kept tight by the easily removable arched piece of thin clock spring slipped between it and the block shown by the heavy dotted line at O.

A fourth gas container would sometimes be convenient for holding extra samples. A fifth space open to the air, through which to examine a bead or to empty the buret, would also be a convenience. In the authors' apparatus there is barely room on the side of the triangular block for this purpose.

Gas samples are stored and transferred by means of suitable capillary pipets, having the same ground tip and shape as the bent portion of the capillary buret with one change. The capillary pipet comes up 1 inch (2.5 cm.) higher than at A, Figure 2, and is then bent down and enlarged for a short distance to give the necessary volume. A strong medicine dropper bulb or a plugged piece of flexible rubber tubing is attached to the end of this enlarged portion. The operation of the pipet is similar to that of the buret.

Reagents

The reagents for oxygen and ammonia as found in the literature—yellow phosphorus and moistened phosphorus pentoxide, respectively—were found to be very slow and the following improvements are recommended: In preparing the phosphorus bead for oxygen, extreme care must be exercised to have it dry because a film of phosphoric acid may increase the time required for reaction as much as a hundred fold. By washing the bead in water, then in alcohol, and then drying it in a stream of dry natural gas, the bead may be made so active that it reacts almost instantly and will even ignite in samples containing much oxygen.

Of several reagents tried, potassium bisulfate was found to be by far the most satisfactory for absorbing ammonia. The bead formed by dipping the platinum loop into the molten salt must be moistened with water and dried in order to leave a surface coated with many fine crystals. The reaction is very rapid and goes to completion. A bead after having absorbed large quantities of ammonia will not increase the volume of a sample of nitrogen when exposed to it.

It was found that a measurable trace of ammonia will adsorb on the walls of the buret. After the ammonia has been adsorbed, if the sample is drawn back into the buret most of this adsorbed ammonia leaves the walls and may be removed by a second exposure to the bead. Careful cleaning of the buret reduces this adsorption but does not eliminate it.

Liquid reagents such as concentrated sulfuric acid may be used with some degree of success if contained in a suitable porous bead (*2*). For such a bead, a mixture of 70 per cent grog and 30 per cent kaolin was used. The grog, ground porous earthenware, was sifted to a uniform size, passing 120- and retained on 140-mesh screen. The kaolin should pass 200-mesh. The consistency of the mixture should be such as to allow it to be dipped up with the platinum wire loop if a smooth surface is to be expected. Only a few minutes' heating in a Fischer burner flame is necessary to bake the bead.

This apparatus is inexpensive, is far less subject to disaster than an Orsat or Burrell, and requires but a fraction of the time to conduct an analysis, yet accuracy is not sacrificed. The operator may sit at a table while conducting analyses.

Acknowledgment

The authors wish to express appreciation particularly to E. P. Schoch who made the work possible, and to W. L. Benson, F. V. Patten, and David McKnight for their helpful assistance and suggestions.

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Determination of Rubber in Rubber-Bearing Plants

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THE determination of the true rubber content of both raw and manufactured rubber has been the subject of extensive investigation. Search has failed to reveal any corresponding record covering studies applicable to rubber-bearing plants. The authors' investigations, covering such methods as have been published, demonstrate their inaccuracy and inadequacy for practical use. There has never been published, as far as the authors have been able to determine, any thorough, systematic study of the factors which determine the value and accuracy of any method for the quantitative determination of the pure caoutchouc contained in a given specimen of plant tissue.

The work embodied in the present communication was undertaken as an essential step towards the solution of some of the complex problems in the production of rubber from the guayule shrub. Without some method for determining with completeness and accuracy in terms of pure caoutchouc[1] the value of any given sample it would have been fruitless to proceed to studies of the metabolism of the plant. The equally important problems in the control of commercial operations, both in field and factory, hinged at the outset on the development of an accurate means to determine the rubber content of the plant.

The authors' method, while primarily developed for the analysis of guayule, has been applied with success to the investigation of other rubber-producing plants. The difficulties encountered and overcome in developing the method for guayule shrub are no different from those which will arise, to a greater or less extent, in the investigation of rubber-bearing plants in general. The authors are indebted to the Intercontinental Rubber Company for permission to make public the results of two years of intensive study of this problem.

At the outset the investigation was limited to methods involving solvent extraction of the rubber from the plant tissue and the direct gravimetric determination of the product. Past experience of the senior author in this field had conclusively demonstrated inherent inaccuracies and uncertainties in alternative methods, such as the determination of the rubber as tetrabromide.

Factors Affecting Accuracy

From the results of study of existing methods it became evident that the problem of the complete extraction of the rubber hydrocarbon from vegetable tissue was not nearly as simple as it might seem (*2, 3, 5, 6*). The methods described in the literature (*1, 7*) resulted either in incomplete extraction with losses from one source or another, or in contamination of the extracted rubber by impurities present in the raw material. The alcohol precipitation method of Fox (*1*), for example, was found to give, with guayule shrub, films contaminated in some instances with as much as 25 per cent of benzene-insoluble impurities. Furthermore, some of the most important factors affecting the accuracy of rubber determinations as applied to plant products have been entirely overlooked. Among those of major importance are:

Respiration changes occurring in the plant tissue after harvesting and before analysis.

The influence of colloidal, protective materials in the plant structure upon the extraction of the rubber.

The effect of the type of rubber solvent used.

The oxidation which occurs during the drying of films of extracted rubber.

Much attention has been directed by Hall and Goodspeed (*2*), Fox (*1*), and others to the influence of fine grinding of the sample upon the completeness of extraction. In the authors' early work considerable time was devoted to an investigation of this question. Later, however, they were able to show that the degree of fineness of grinding of the material for analysis is of relatively minor importance when account is taken of other factors, more particularly of the breaking down and removal of the protective colloids before extraction of the pure rubber. The finest of grinding is no substitute for this.

That changes are continually going on in plant products after harvesting is generally recognized. In some fields these changes have been studied in great detail and are of the utmost importance, but in the handling of rubber-bearing plants for analysis they have apparently been overlooked. Many of the anomalous results of past analyses may be traced, without doubt, to the failure to appreciate the extent of such respiration changes.

The evolution of carbon dioxide and water vapor, with consequent loss of dry weight, which takes place in the ordinary course of respiration in plant products stored under favorable conditions, results in fictitiously high values for the rubber content of the parent material. Losses of more than 15 per cent in the dry weight of the original material have been found to occur in the few days elapsed between pulling and analysis of guayule shrub.

This emphasizes the necessity for careful storage prior to analysis. The authors' studies have shown that desiccation to less than 9 per cent moisture content or storage of the freshly ground material, ready for analysis, in tightly packed and stoppered jars, is an effective means for preventing this loss in weight.

In addition to the apparent increase in rubber in the sample, brought about by the more or less rapid disappearance of materials other than rubber by decomposition in storage, there may be a real increase in the amount of rubber extracted by the published methods of analysis from shrub in which such changes have taken place. But this, again, is due entirely to the inadequacy of the analytical methods in use. These methods have not taken into account the influence of materials present in the plant which seriously interfere with the extraction of the rubber itself. The decomposition of these plant materials by respiration in storage facilitates the subsequent extraction of the rubber by solvents.

It is obvious that if account is not taken of this fact, the rubber value of a sample will depend upon the time and conditions of storage. This was the situation found in connection with guayule. Years of recorded results obtained by the older methods of analysis tended to show consistently that the percentage of rubber in the guayule plant increased by storage after harvesting. Similarly, the increase in the rubber content of Chrysothamnus plants during storage, reported by Hall and Goodspeed (*2*), will undoubtedly find its true explanation in

[1] The terms "pure caoutchouc" or "pure rubber" used throughout refer to the ultimate product of analysis which not only resembles rubber in all its physical characteristics but also bears the empirical formula $(C_5H_8)_n$, as determined by analysis.

changes and losses in materials other than rubber brought about by respiration processes going on in the sample before analysis.

The influence of other plant products (hemicellulose, pectins, proteins, etc.) within and without the cell wall upon the extractability of the rubber has nowhere been given sufficient consideration. Acetone extraction to remove fats, resins, etc., has been generally applied. But the authors' studies have shown that the presence of these other materials

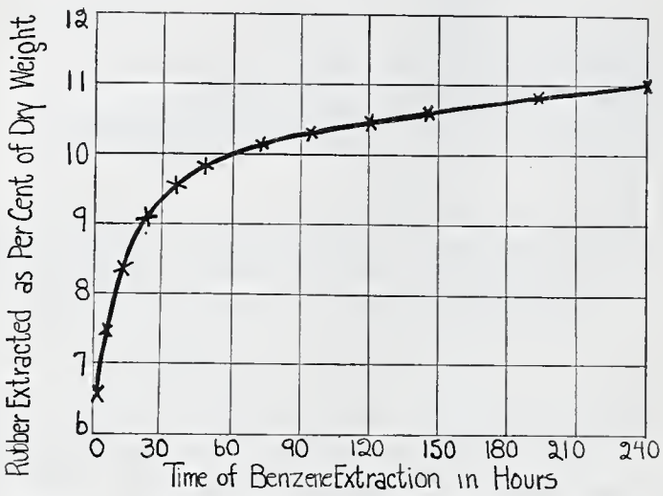

FIGURE 1. RUBBER EXTRACTION OF GUAYULE SHRUB

Samples extracted with water and acetone before determination of rubber.

has a much more profound influence upon the completeness of extraction than the constituents of the acetone extract. Mere water leaching, as suggested by Whittlesey (*7*), is entirely inadequate. A slow hydrolysis in fact occurs during the leaching operation, but the complete removal of water-soluble materials from the plant by such means is a matter of months and quite impossible as a practical matter.

Very drastic treatment is required to break down those materials which prevent the complete extraction of the rubber itself. Much time was devoted to the study of this problem before a satisfactory method, involving hydrolysis by dilute acid under steam pressure, was evolved. Even this is insufficient unless followed by a thorough removal of all the products of hydrolysis prior to extraction of the rubber.

The results in this connection all tend to show that the difficulties in the way of complete extraction of rubber from plants are not due, as has been at times thought, to either cell wall hindrance or to insoluble modifications of rubber. Rather it is the presence of other materials, colloidal in character, which seems to prevent the solution of the rubber. This is somewhat analogous to the effect of gelatin in raw rubber, 10 per cent of which mechanically incorporated (by milling) renders raw rubber very difficult of solution in benzene.

The choice of solvent used for rubber extraction has generally been left entirely open. The authors' experience has proved, however, that this is a matter of no small importance. Carbon tetrachloride is a conspicuous example of a solvent which has been widely advertised and much recommended for extraction purposes in general because of its noninflammability. But the decomposition to which it is subject, in the presence of light, makes it entirely unsuitable for accurate quantitative work (*4*). Chlorination of the rubber in the process of extraction takes place accompanied by the formation of nonvolatile residues from the solvent itself, which are an even more serious source of error. The use of so-called pure carbon tetrachloride for extraction purposes over some period of time resulted in values for the authors' rubber estimations which were never less than 10 and sometimes 15 per cent too high.

These same errors are introduced in varying degree by all the chlorinated hydrocarbon solvents investigated. With the more stable ones, such as dichloroethane, the errors are reduced, but in all cases the uncertainty involved makes the use of a stable solvent such as benzene strongly recommended.

The universal practice in all published methods of rubber determination of this class includes drying the film of extracted rubber in the air. The error due to oxidation of the rubber under these conditions has been more or less ignored. But such thin films of rubber, being free from the protective agents present in the plant, are extremely susceptible to oxidation. An increase of more than 10 per cent in the weight of a film may easily be due to this source.

Neither vacuum drying nor the use of inert gases offers a solution of the difficulty in practical routine work. The former is excessively slow and the latter exceedingly cumbersome.

Experience with antioxidants suggested their possible application to analytical practice to overcome this difficulty. The authors have been able to show that antioxidants of the proper type are very effective in preventing the oxidation of thin films of pure rubber obtained from plant extracts by their method. Very small amounts of dimethyl-*p*-phenylenediamine, for example, are capable of protecting the rubber during the severest overdrying. Added in a standard benzene solution to the rubber extract before evaporation, this offers a convenient means for eliminating the oxidation error.

It is the authors' belief that such use of antioxidants in analytical procedure should be capable of wide application in other fields of research where organic compounds of great susceptibility to oxidation are encountered.

With the foregoing major explanations the reasons for the various steps in the authors' method of analysis for rubber-bearing plants will be at once clear. Simplification has been sought wherever possible without sacrifice of accuracy, but

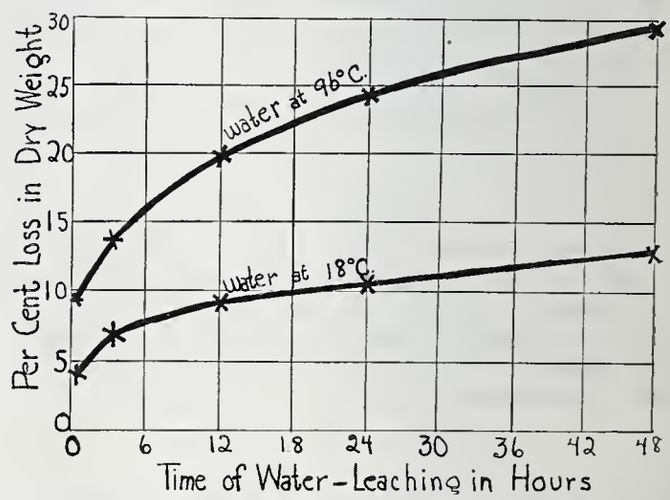

FIGURE 2. RATE OF WATER EXTRACTION OF GROUND GUAYULE SHRUB

in the case of guayule shrub, attempted short cuts have been fatal from the standpoint of complete extraction. Laborious fine grinding has been eliminated. An analysis may be completed in 48 hours and in routine work two men may handle fifty analyses daily.

The accuracy of the method is shown by repeated treatments of the extracted residues from the first analysis, which fail to show the slightest trace of residual hydrocarbon, attesting the completeness of extraction; by tests on a large number of samples by independent workers, which have given results agreeing within 0.2 per cent; and by the purity of the extracted rubber.

That the material extracted from the plant tissue by this method is pure rubber is indicated not merely by its physical

characteristics (a colorless, transparent, elastic film) but also by its chemical reactivity toward sulfur, bromine, etc. The figures for analysis (by combustion) of the extracted films point clearly to a hydrocarbon of the composition $(C_5H_8)_n$ of India rubber. The rather remarkable absence, in fact, of any appreciable amount of oxygen and the complete absence of nitrogen in the films of rubber obtained in daily practice from guayule shrub make both material and method ready means for the preparation of pure, protein-free rubber.

Experimental

It should be unnecessary to point out that proper precautions to insure a uniform and representative sample precede any analytical work. As the authors were confronted with sampling problems ranging from two or three irreplaceable plants to fields of hundreds of acres, the difficulties in this phase of the subject were forcibly impressed upon them. The work involved in developing accurate methods which would give the true rubber content for such cases has no place in the present discussion. It is mentioned merely to emphasize the fact that with variable plant products the method of sampling is of equal importance with the subsequent analytical procedure.

Preparation of Sample

Certain precautions are necessary in the handling of rubber-bearing plants if respiration losses are to be prevented where there is, for any reason, a delay between harvesting and analysis. The importance of this is well illustrated in Table I.

Table I. Effect of Respiration Losses upon the Extractable Rubber in Guayule Shrub

(5-gram samples leached with hot water and acetone, then extracted 24 hours with benzene)

Treatment of Shrub	Time of Treatment	Loss in Dry Weight in Treatment	CO_2 Evolved during Treatment	Moisture Content When Analyzed	Rubber Extracted Actual dry basis	Rubber Extracted Original[a] dry basis
	Days	%	%	%	%	%
Analyzed immediately	None	None	None	39.5	9.2 9.2	9.2 9.2
Same, chopped plants kept in flask covered with watch glass at room temperature	4	4.7	Not determined	42.4	11.0 11.4 11.4	10.5 10.9 10.9
Chopped plants kept in flask at 40° C. and slow current of moist air passed through	5	16.0	7.2	41.0	14.0 14.1	11.8 11.8
Finely ground shrub kept in open at room temperature	7	1.1	Not determined	18.8	9.3 9.5	9.2 9.4
Same packed tightly in glass-stoppered bottle and kept at room temperature	89	None	None	35.3	8.9 9.3	8.9 9.3
Finely ground shrub, vacuum dried, kept in open jar at room temperature	89	None	None	8.6	9.1 9.2	9.1 9.2

[a] After correction for loss in dry weight.

The differences between the results in the last two columns of Table I represent the increase in the per cent of rubber resulting from the loss through respiration of non-rubber materials in varying amounts brought about by different conditions of storage. This table also shows how the usual methods of analysis, in which no provision is made for the complete removal of all colloidal materials interfering with the extraction of the rubber, may give real increases in the amount of rubber extracted from shrub stored prior to analysis. These increases are a function of the respiration changes as measured by the loss in dry weight of the samples. When such elimination of extraction-inhibiting materials is provided for in the method of analysis, no increase in rubber is obtained by aging, as shown by Table II.

Table II. Comparative Effect of Respiration and Steam Hydrolysis in Increasing the Extractability of Rubber from Guayule Shrub

Treatment of Sample before Analysis	Method of Analysis	Loss of Dry Weight in Treatment	Extracted Rubber Actual dry basis	Extracted Rubber Original dry basis
		%	%	%
Analyzed at once	Water, acetone, and benzene extraction	None	10.4 9.7	10.4 9.7
Same; chopped plants incubated at 40° C. in saturated atmosphere with slow current of air for 7 days.	Same	5.1	12.9 12.7	12.3 12.1
Analyzed at once	Hydrolyzed by steaming 3 hours at 30 lbs. pressure, then extracted as above	None	13.2 13.3	13.2 13.3
Incubated 7 days at 40° C. in slow current of saturated air	Same	6.4	14.4 14.5	13.4 13.5
Same, except hydrolyzed before incubation	Same, except incubated between hydrolysis and extraction	None	13.0 13.2	13.0 13.2

The increasing amounts of rubber extracted from samples of increasing fineness by the usual published methods of analysis are shown by Table III.

Table III. Effect of Fineness of Grinding upon the Extraction of Rubber from Guayule Shrub

(5-gram samples leached with hot water and acetone, then extracted with benzene for 24 hours)

Fineness of Grinding	Benzene Extract (Per cent of dry weight of shrub) Without hydrolysis	Benzene Extract (Per cent of dry weight of shrub) Acid hydrolysis under steam pressure
Coarse. Slivers about 9.5 mm. long ranging down to pieces 1.6 mm., with many lumps.	10.1 10.7	14.5 14.4
Medium. A few slivers 6.4 mm. long but most pieces about 3.2 mm. ranging down to some very fines. (All pass 14 mesh.) No lumps.	11.9 12.3	14.2 14.3
Fine. A very few slivers 3.2 mm. long but most pass 30 mesh. Some lumps of rubber.	12.8 13.0	14.1 14.3
Regrinding. Residue from fine grinding above; reground after first analysis until all passes 50 mesh.	0.6 0.8	None
Total for fine sample, reground, average	13.6	14.2

Even with the finest grinding practicable with guayule shrub, more and more rubber may be removed by increasing the time of extraction, as is clearly brought out by Figure 1. But such extremes of fine grinding are unnecessary when the proper analytical procedure, involving hydrolysis, is followed, as demonstrated by Table III. Moreover, owing to the high rubber content of guayule shrub, extremely fine grinding is impractical because of the tendency of the rubber to agglomerate under mechanical working. For this reason a fineness of about 14 mesh which gives a uniform sample has been adopted. With other plants of lower rubber content, the hydrolysis process will eliminate the tedious grinding to 100 mesh or more which has been recommended.

Removal of Colloidal Protective Materials

It has already been pointed out that drastic treatment is necessary to insure the complete breaking down and removal of materials which otherwise interfere with the accuracy and completeness of the rubber extraction. The slow hydrolysis

which goes on in the ordinary water-leaching of guayule shrub is shown in Figure 2. The relationship between the removal of materials which are water-soluble or which may be rendered so and the rubber extracted is brought out by Table IV.

Table IV. Relation between Water-Soluble Material Removed and Rubber Extractable from Guayule Shrub

(Acetone extraction 12 hours, benzene extraction 24 hours)

Method of Removing Water-Soluble Material	Water-Soluble Materials Removed (By difference)	Acetone Extract	Benzene Extract
	%	%	%
2 hours' leach with water at 60° C.	6.2	5.9	8.5
		6.0	8.6
3 hours of steaming at 30 lbs. pressure (2.1 kg. per sq. cm.) followed by leaching as above	23.1	6.4	8.7
		6.6	9.0
Steaming as with preceding sample, followed by 6 hours of leaching at 132° C.	30.7	6.0	9.2
		6.3	9.4
Same as preceding, except 1% sulfuric acid used for leaching	49.4	6.9	10.0
		7.0	10.3

All results based on dry weight of sample

Some of the studies made to determine the optimum conditions of acid concentration, and time and temperature of steaming required for complete rubber extraction are shown in Tables V and VI. It was from such results as these that 3 hours of boiling with 1 per cent sulfuric acid followed by 3 hours of steaming at 122° C. was adopted for the hydrolysis treatment in the final method.

Table V. Effect of Acid Concentration and Time in the Hydrolysis of Guayule Shrub Prior to Rubber Extraction

(All samples steamed 6 hours at 30 pounds per sq. in. pressure (2.1 kg. per sq. cm.) after acid treatment and then extracted with hot water 3 hours, acetone 12 hours, and benzene 24 hours)

Concentration of Sulfuric Acid	Time of Boiling with Acid	Rubber Extracted (Based on dry weight of sample)
%	*Hours*	%
None	None	8.31–8.74
0.5	3	9.44–9.47
0.5	6	10.04–10.11
1.0	1	9.81–9.99
1.0	2	10.63–10.85
1.0	3	10.76–10.90
1.0	6	10.75–10.88
2.0	1	10.01–10.53
2.0	3	10.62–10.90
2.0	6	10.77–10.95
3.0	1	10.58–10.76
3.0	3	10.70–10.92
3.0	6	10.68–10.82

That the complete removal of such materials after they have been rendered water-soluble is absolutely necessary for complete rubber extraction is illustrated by Table VII. Clearly it is not only the hydrolysis which is important but the removal of materials which interfere with the extraction of the rubber. This has been provided for in the analytical method finally adopted by 3 hours of leaching with hot water after hydrolysis.

Table VI. Effect of Time and Temperature of Steaming on Extractability of Rubber from Guayule Shrub

(All samples treated with boiling 1 per cent sulfuric acid for 3 hours before steaming and after steaming extracted with hot water 3 hours, acetone 12 hours, and benzene 24 hours)

Temperature of Steaming	Time of Steaming	Rubber Extracted (Based on dry weight of sample)
° *C.*	*Hours*	%
...	None	8.0–8.1
98	3	10.2–10.4
	6	10.0–10.1
	9	11.5–11.5
	12	11.5–11.7
122	1	10.1–10.3
	2	10.0–10.5
	3	11.3–11.6
	6	11.1–11.4
153	3	11.6–11.6
	6	11.4–11.5
162	1	11.2–11.4
	3	11.4–11.5

Table VII. Effect of Presence of Water-Soluble Materials upon Extractability of Rubber from Guayule Shrub

(All samples extracted 12 hours with acetone and 24 hours with benzene)

Treatment of Samples	Rubber Extracted (Based on dry weight of sample) After leaching 3 hours with hot water	Without water leach	Difference Due to Removal of Water-Solubles
	%	%	%
No hydrolysis	7.9–8.2	8.0–8.3	1
Steam hydrolysis	9.5–9.8	8.6–8.4	10

Choice of Rubber Solvent

The error introduced by the use of such solvents as carbon tetrachloride may be clearly seen from Table VIII.

In the decomposition of carbon tetrachloride which takes place in the light in the presence of air the odor of carbonyl chloride was detected. The chlorination of the rubber produced by the more stable dichloroethane clearly indicates the advisability of using benzene as a solvent for accurate quantitative work unless the determinations are carried out in the dark.

Prevention of Oxidation

The importance of protecting the rubber after extraction against oxidation, during drying, in preparation for weighing has been emphasized. The extent of the error introduced by the usual air-drying is shown by Table IX which also illustrates the way in which dimethyl-*p*-phenylenediamine may be used to overcome this difficulty. Details of procedure

Table VIII. Effect of Solvent on the Rubber Values of Guayule Shrub

(All samples boiled 3 hours with 1 per cent sulfuric acid and steamed 3 hours at 30 pounds per sq. in. (2.1 kg. per sq. cm.) pressure, then extracted with hot water 3 hours, acetone 12 hours, rubber solvent 24 hours)

Solvent Used (150 cc. in each case)	Method of Extraction	Total Weight of Extract	Weight of Residue from Solvent (Determined in blank) Before extn.	After extn.	Chlorine in Rubber (approx.)	Rubber Extract (Based on dry weight of shrub sample) No corrections	Corrected for residue from solvent
		Mg.	*Mg.*	*Mg.*	%	%	%
Carbon tetrachloride (purified)	In the dark	424	000	000	..	11.2	11.2
		433				11.5	11.5
Same	In diffused light	443	000	19	0.9	11.8	11.2
		452			1.1	12.1	11.5
Same	In direct sunlight	469	000	42	Not	12.4	11.3
		481			estimated	12.7	11.6
Same, except crude from reagent bottle	In dark	460	30	30	Not	12.3	11.4
		462			estimated	12.3	11.4
Same	In diffused light	459	30	39	2.9	12.1	11.1
		470			3.5	12.4	11.4
Same	In direct sunlight	506	30	82	Not	13.4	11.2
		521			estimated	13.8	11.6
Dichloroethane (from reagent bottle)	In diffused light	442	...	...	0.21	11.7	..
		450			0.23	11.9	
Benzene (c. p.)	In diffused light	422	000	000	0.0	11.2	11.2
		428				11.4	11.4

adopted to this end are to be found in the description of the method given below.

Table IX. Oxidation of Rubber Films during Drying

(All samples obtained by standard acid hydrolysis and steaming treatment of guayule shrub followed by extraction with hot water, acetone, and benzene)

Method of Drying	Time of Drying: 24 hours Weight of film	24 hours Extraction (Based on dry shrub)	48 hours Weight of film	48 hours Extraction (Based on dry shrub)
	Mg.	%	*Mg.*	%
In flask open to air in oven at 105° C.	674 676	15.0 15.0	701 705	15.6 15.7
In closed flasks through which current of nitrogen at 105° C. was passed	629 637	14.0 14.1	634 639	14.1 14.2
In flask open to air in oven at 105° C. but in presence of 7 mg. of dimethyl - *p* - phenylene diamine. (Results corrected as determined in blank)	628 632	14.0 14.1	631 638	14.1 14.2

Accuracy of Method

The two criteria of accuracy in the determination of the true rubber value of a plant product are both met by the present method. First, the extraction of the rubber is complete as evidenced by the failure of repeated treatments, even after regrinding of the sample to a fine mesh, to remove the slightest trace of additional rubber. This is to be contrasted with the results obtained with the usual methods which do not include hydrolysis treatment as shown in Figure 1 and Table III. Second, the rubber extracted and weighed in the final determination is entirely free from impurities. The unusually good agreement between the carbon and hydrogen values for the rubber extracted by this method from guayule shrub (when dried in nitrogen), with the theoretical values for C_5H_6, is shown by Table X. In addition, qualitative tests gave negative results for nitrogen, sulfur (thought possible as a result of the acid hydrolysis treatment), and ash.

Table X. Combustion of Rubber Obtained from Guayule Shrub by Acid Hydrolysis, Steaming and Extraction with Benzene

(Rubber films dried in a current of pure dry nitrogen)

	Carbon	Hydrogen	Total
	%	%	%
Theory (C_5H_6)	88.22	11.78	100.0
Sample A	88.00	11.75	99.75
Sample B	88.09	11.68	99.77
Sample C	88.15	11.41	99.56

Description of Method

The following is a detailed description of the method as finally adopted for the routine handling of as many as fifty samples a day of guayule shrub by two experienced operators:

Preparation of Sample. The plants to be analyzed, washed free of adhering soil, are first coarsely crushed by two passes through corrugated differential laboratory mill rolls set up as tightly as possible. This material is then ground successively with a Universal grinder and a corn mill. (Made by Landers, Frary, and Clark, New Britain, Conn. The use of an attrition-type mill operated with a reciprocating motion for the finer stages of grinding has proved effective in preventing the agglomeration of the rubber in guayule shrub.) After each stage of grinding the shrub is thoroughly mixed and quartered by means of Jones ore samplers of various sizes. The final quarter is divided into two lots of a little more than 5 grams each and one lot of approximately 10 grams. The remaining shrub is preserved, packed tightly in an airtight glass jar, in case of emergency.

Duplicate 5-gram samples are then weighed out on the analytical balance from the small samples divided out with the sampler. These are transferred to Coors porcelain extraction thimbles, which for convenience are 22 mm. in diameter by 70 mm. high, inside measurements, with 2-mm. perforations in the bottom. A thin layer of wool batting is placed below and above the shrub to prevent loss.

The moisture content of the sample is determined at the same time by vacuum-drying the 10-gram sample at 110° C. in a Petri dish.

Removal of Water-Solubles. The samples in the porcelain thimbles are boiled in a 1 per cent solution of sulfuric acid for 3 hours. For this operation it has been found convenient to use a monel metal bath provided with a water-sealed lid and water-cooled condenser outlet to maintain the acid concentration. A punched plate is employed to hold the thimbles upright on a monel metal screen. After 3 hours the samples, still saturated with acid, are transferred, along with the supporting tray, to an autoclave where they are steamed for 3 hours at 30 pounds per sq. in. (2.1 kg. per sq. cm.) pressure.

For the subsequent operation of leaching to remove the materials rendered water-soluble by the preceding treatments, a copper bath has been found convenient in which the thimbles are held upright by holes in the lid and are supported on a wire screen 4 cm. from the bottom. Water at 60° C. from a storage-type electric water heater is run through each thimble individually in a slow stream. Three hours of leaching are sufficient completely to remove all water-soluble materials. The amount of material thus removed can be determined quantitatively with fair accuracy, by difference, by weighing the thimbles before and after the completed analysis.

Acetone Extraction. After water-leaching, the thimbles are immediately placed in siphon cups of the Underwriters' Laboratories type and are extracted for 12 hours (on an electric hot plate) using about 150 cc. of acetone. If the water-solubles are to be determined, as above, this extraction must, of course, be made in a tared flask.

Extraction of Rubber. The acetone left in the sample from the preceding operation is first removed by heating the thimbles in the vacuum oven for about half an hour. The rubber is then extracted with 150 cc. of benzene in the usual way. At least 16 hours are required for this operation.

Drying of Rubber. The benzene extract of the shrub is evaporated, dried, and weighed in the same tared flask used for the extraction. Before evaporation 5 cc. of a 0.1 per cent solution of dimethyl-*p*-phenylenediamine in benzene is pipetted into the rubber solution. A correction, based upon a blank determination, is made for this material in calculation of the results. The rubber solution is evaporated on a water bath and then dried to constant weight in a Freas oven at 105° C. Overnight drying has been found very convenient for this last step. The flask is finally weighed to three decimal figures. Accuracy to three significant figures in the final result expressed as a percentage of the dry weight of the sample has been found sufficient for all purposes.

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Increased Trade in Tanning Extracts. That the trend in international trade in tanning products is toward increased purchases of tanning extracts and reduction in purchases of raw products is revealed in a survey recently completed by the Commerce Department. International trade in tanning extracts during 1932 totaled nearly 310,000 tons as compared with 270,000 tons in the preceding year. Quebracho continued to be the most important tanning extract in international trade, accounting for approximately 75 per cent of total exports of tanning extracts. Argentina supplied almost the entire amount of this item, making shipments to all parts of the world, with the United States the chief purchaser.

Evaluation of Textile Penetrants

An Improved Centrifugal Method

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An improved centrifugal method for the evaluation of textile penetration assistants is described. The advantages of this method as compared with the sinking-time method for the quantitative evaluation of wetting-out agents are pointed out. It is shown that the surface tension of a solution toward air is no criterion of its penetrating ability toward textile fibers. Measurements of the efficiency of a variety of textile assistants as penetrating agents over a range of concentrations and temperatures are given.

THE recent wide use of a variety of synthetic organic chemical products, as assistants in the penetration of textile fibers by liquids, has led to a considerable interest in the quantitative evaluation of the efficiency of these substances. The penetration of textile fibers is assisted by two classes of materials, solvents which remove the obstructions to penetration, and surface-active materials which greatly reduce the tension at interfaces and act as colloidal penetrating assistants. This paper is concerned only with the surface-active materials. The action of solvent penetration assistants in aiding in the entrance of solutions into fibers requires no discussion, but the action of the colloidal penetrants is complicated by a number of factors which require study. No attempt is made to throw light on the mechanism of the action of penetrants, but a method for the practical evaluation of surface-active, or colloidal, textile penetrants is described.

It is necessary to examine a system in which the textile fiber, surrounded by oils and waxes together with a layer of sorbed gases, is in contact with a solution of the penetration assistant. If the solution is to penetrate the fiber it must displace this gas, emulsify the waxes and oils sufficiently to gain access to the material, and diffuse throughout the fiber by means of capillary forces. The evaluation of a penetration assistant is an evaluation, directly or indirectly, of the tension of the solution at the interface liquid–adsorbed gas, as well as of the tension at the interface liquid-solid (fiber); and of the emulsifying action of the solution on the waxes and oils of the fiber.

A number of methods for the evaluation of textile penetration assistants have been reported in the literature, but many are obviously capable of giving only a qualitative measure, while others are limited through their failure to measure all the factors involved. The methods may be divided roughly into three groups:

1. Measurements of the forces acting at the surface of the solutions.
2. Determinations of the time taken for a substance to wet-out and sink in a solution.
3. Measurement of the quantity of liquid absorbed during a given period of time by the fiber.

Kind and Auerbach (*7*) made comparisons of wetting agents by measuring the drop number of solutions of the assistants. Herbig and Seyferth (*6*) made observations of the capillary rise in threads of yarn suspended under standard conditions in solutions of the wetting assistants. Auerbach (*1*) used as a method of evaluation the measure of the time required for a square of fabric floating on the surface of the liquid to become wet-out and sink. Ristenpart and Petzold (*9*) measured the time required for a submerged strand of the fiber to become sufficiently wet-out to sink, while Draves and Clarkson (*2*) measured the time required for a submerged skein to become sufficiently wet-out to sink when attached to a 1.5-gram weight. Herbig and Seyferth (*4, 5*) wet-out yarn and centrifuged it under standard conditions in order to obtain a measure of the amount of water absorbed. Seck and Lachmann (*10*) immersed a weighed piece of cloth in a solution for a definite time, and after draining calculated the amount of solution absorbed from the gain in weight of the cloth.

Comparisons of wetting assistants based on determinations of the surface tension of their solutions do not take into consideration the interfacial tension and the forces of capillary attraction involved. Methods based on the capillary rise in a thread dipping into a solution of the assistant are stated by Herbig and Seyferth (*6*) to lead to conclusions contradictory to observations made in actual commercial practice. Methods which involve sinking-time measurements are frequently erratic in their performance since they depend upon the interface liquid–adsorbed gas, the behavior of which may be readily influenced by both the temperature and the viscosity of the solution. A method involving the use of a centrifuge to remove extraneous solution from the wet fibers appears much more likely to give uniformly reproducible results than does a method which relies upon the draining of the liquid from the fabric.

The method of Herbig and Seyferth (*4, 5*) has certain defects which tend to render questionable any conclusions of a quantitative nature based on its use. Stöcker (*11*) has pointed out that large errors are introduced as a result of the procedure employed by Herbig because of the relatively long time interval between the wetting of the yarn and the subsequent centrifuging process. He also states that Herbig's immersion time is too short to give results of any significance. The work reported in this paper has eliminated the source of error pointed out by Stöcker, placed the method on a sound basis, and established a method of testing that will be of significance in industrial problems.

The primary function of any good textile penetration assistant is the production of a thorough and rapid penetration of fibers by a solution. It is of importance in the evaluation of textile penetration assistants to know the actual degree of saturation of the fiber with a solution—i. e., the extent to which the solution has penetrated into the fiber—at various time intervals during the wetting-out process, as well as to know the moisture content of a fiber when it is wet-out. These data, together with stability data, are needed to evaluate the worth of penetration assistants.

OUTLINE OF METHOD

Textile penetration assistants are most widely used in the processing of cotton. Most of the work with the centrifugal method has been confined to a study of cotton yarn. However, the method is applicable to other vegetable and to animal fibers. The cotton fiber used was in the form of skeins prepared from unbleached, unboiled-out cotton yarn (40/2) of the type which is extensively used in the testing of dyestuffs. This yarn contained moisture which had been ab-

sorbed from the atmosphere, but several months' experience indicated that the validity of the results was not seriously impaired by the initial quantity of moisture present in the air-dry yarn provided the yarn was of uniform quality.

A skein of the raw cotton yarn, approximately 5 grams in weight, was weighed to the nearest centigram. The yarn was pulled tight several times in order to line up the strands, then doubled to form a loop of half the original length, and attached to an anchor. The skein was cut open at the top of the loop by means of shears and struck on the palm of the hand 8 to 10 times in order to separate and free the individual strands. This preparation produces uniformity in the physical condition of the skeins, while the shearing of the yarn facilitates the rapid expulsion of adsorbed air by the solution as it penetrates the fibers. The skein and anchor were dropped into a cylinder containing a solution of the penetration assistant at a known concentration. The yarn was immersed in this solution for a time, measured on a stopwatch graduated to read to fifths of a second, and was then transferred to the slowly revolving basket of a centrifuge by pouring the entire contents of the cylinder into the basket. The centrifuge used was a hand machine with a gear ratio of 1 to 36 and a basket radius of 5.5 cm. Since the time of contact of the yarn with the liquid is an important factor in this test, care was taken that the skein dropped from the cylinder into the basket with a variation of only a few fifths of a second from the desired wetting-out time. Within one second after the transfer of the skein, the speed of the slowly rotating basket was brought to approximately 2160 r. p. m. and the extraneous solution was removed. The basket was revolved at this velocity for the desired time and then stopped quickly by means of a braking force. The skein was removed, detached from the anchor, and weighed in a weighing bottle. The quantity of solution retained by the yarn was expressed in terms of the initial weight of the skein.

The amount of solution in the yarn after this treatment is indicative of the amount of water absorbed. The percentage of moisture absorbed is a relative figure which depends entirely upon the length of the wetting-out time and the conditions employed in the centrifuging procedure. For this reason it is necessary to adopt a standard procedure that will give results which can be reproduced with reasonable accuracy and which at the same time will remove a minimum quantity of the solution actually absorbed by the fibers. To study the various conditions which can be employed and to select a proper testing procedure, a series of tests were made with solutions of a commercial alkylated naphthalene sodium sulfonate (product A) over a range of concentrations with a variation in the immersion time of from 15 to 60 seconds and in the centrifuging time of from 10 to 30 seconds. Five determinations were made at each concentration for each specified variation. Summary of the data is given in Table I.

Table I. Penetration Tests on Cotton with Product A Solutions in Water at 25° C.

	Water Absorbed				
Concn., *G./l.*	%	%	%	%	%
Immersion time, seconds:	60	30	30	15	15
Centrifuging time, seconds:	30	30	10	30	15
0.0	27.4	21.1	24.6	..	..
0.1	29.6	29.5	27.5	23.5	25.6
0.2	36.1	34.0	33.1	29.8	29.5
0.5	50.1	45.0	48.9	38.1	41.5
1.0	64.9	55.8	68.8	50.1	53.2
2.0	68.3	64.0	80.3	62.5	71.7
3.0	65.1	66.1	86.2	67.4	78.2
5.0	69.9	66.1	88.3	72.4	82.7

As a result of the above tests a standard wetting time of 15 seconds and a standard centrifuging time of 15 seconds were adopted. The immersion time of 15 seconds is sufficiently long for a good wetting agent to show pronounced activity at concentrations ordinarily used in commercial practice, while the results obtained by centrifuging the yarn for 15 seconds are sufficiently reproducible to permit a definite distinction to be made in the activity of the solutions at different concentrations of the penetration assistant. To illustrate the variation to be expected between individual determinations, detailed information on experiments at four different concentrations of product A is given in Table II.

While the individual determinations of a given series in Table II show considerable variation, the mean averages obtained represent reasonably accurate evaluations of the quantity of solution retained by the cotton fibers. The probable error in the mean average of a series has been determined by the equation (*3*)

$$\text{Probable error} = 0.6745 \sqrt{\frac{\Sigma d^2}{n(n-1)}}$$

where Σd^2 is the sum of the squares of the deviations of the single observations from the mean. It was found that the probable error in the mean average was in each case less than 1.5 per cent. The results are represented graphically in Figure 1 with logarithms of the concentrations plotted as abscissas and logarithms of the average per cent absorption plotted as ordinates. It is observed that a smooth curve can be drawn through the points plotted.

Table II. Penetration Tests with Solutions of Product A in Water at 25° C.

Trial	Weight of Skein	Water Absorbed	
	Grams	*Grams*	%
	Concentration 1.0 gram per liter		
1	5.05	2.59	51.3
2	5.00	2.71	54.2
3	5.09	2.64	51.9
4	5.07	2.73	53.8
5	5.11	2.80	54.7
		Av.	53.2
	Concentration 2.0 grams per liter		
1	5.11	3.53	69.1
2	5.09	3.89	76.4
3	5.19	3.79	73.0
4	5.11	3.48	68.1
5	5.15	3.71	72.0
		Av.	71.7
	Concentration 3.0 grams per liter		
1	5.04	3.67	72.8
2	5.11	3.71	72.6
3	5.11	4.22	82.6
4	4.97	4.03	81.1
5	5.10	4.18	81.9
		Av.	78.2
	Concentration 5.0 grams per liter		
1	5.15	4.45	86.4
2	5.14	4.00	77.9
3	5.11	4.37	85.4
4	5.08	4.32	85.0
5	5.00	3.95	79.0
		Av.	82.7

Application of Method

The method was applied to a study of a variety of chemical types of penetration assistants which represent the most important commercial products on the market at present.

Product A is a dialkylated naphthalene sodium sulfonate of 85.25 per cent strength.

Product B is a sodium lauryl sulfate product of 71.1 per cent strength prepared from technical lauryl alcohol.

Product C is a sodium oleyl sulfate product of 48.4 per cent strength prepared from technical oleyl alcohol of iodine number 50.

Product D, which contains 39.7 per cent of active constituent, is a condensation product of oleic acid or oleyl acid chlorine with taurine.

The soap used was a sodium oleate soap containing 79.4 per cent of fatty acid salts.

Penetration Efficiency of Water Solutions

Tests of the wetting-out efficiency of solutions of these products were made over a range of concentrations at 25°, 49°, and 93° C. A summary of the results obtained is given in Table III, while graphical representations of the data at 25° and 49° C. are given in Figures 2 and 3. Each value given in this table represents an average of five experimental determinations.

The data given in Table III show that, with the exception of solutions of product C, the actual efficiency of the solutions

Table III. Water Absorbed by Cotton Yarn at 25°, 49°, and 93° C. from Solutions of Textile Penetration Assistants

Concn.	Product A			Product B			Product C			Product D			Soap		
	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.	25° C.	49° C.	93° C.
G./l.	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
0.0	24.0	20.9	67.5	..	23.1	..	..	..	..	..	19.2	..	..	25.5	..
0.1	25.6	27.8	..	27.4	31.9	..	..	..	..	..	22.5	..	27.9	34.3	..
0.2	29.5	36.3	..	33.2	40.6	..	..	..	..	30.9	28.8	..	33.6	35.0	..
0.5	41.5	44.2	69.0	52.2	55.6	64.4	36.3	50.8	70.1	43.1	48.7	62.1	50.8	52.1	64.9
1.0	53.2	52.6	..	69.1	68.9	68.3	45.6	61.0	..	55.0	57.4	..	66.4	60.1	..
1.5	..	..	..	..	..	..	..	..	..	..	..	..	..	72.0	..
2.0	71.7	64.0	..	81.2	73.1	68.9	..	73.9	..	68.7	69.0	..	79.5	73.9	..
3.0	78.2	70.6	65.1	83.6	74.4	67.3	59.4	74.6	72.9	..	..	65.4	85.2	81.5	75.9
4.0	..	..	..	..	..	..	..	..	..	74.8	..	..	..	..	..
5.0	82.7	71.5	..	81.5	73.3	..	66.1	77.0	..	..	70.8	..	94.1	88.9	..
6.0	..	..	..	..	..	..	..	..	..	78.0	..	..	..	..	..
7.5	..	..	..	..	..	..	..	..	..	..	69.4	..	94.7	87.0	..
8.0	..	..	..	..	..	..	..	..	..	79.4	..	..	..	..	..
10.0	..	72.3	..	..	..	..	77.9	75.2	..	82.0	73.0	..	90.7	85.9	..

of wetting-out agents studied decreases with increase in temperature. The surface activity of these solutions decreases as the temperature increases and this decrease in surface activity leads to the conclusion that these colloidal penetration assistants pass into molecular solution as the temperature is increased. On the other hand, solutions of product C are shown to exhibit decidedly superior penetrating qualities at the higher temperatures. Solutions of product C are particularly effective at 49° C. but still show some superiority even at 93° C. Lenher (*8*) has shown that the micelles of product C are too large to produce their maximum effect at 25° C. A dispersion of the micelles at high temperatures into more effective sizes would account for the marked increase noted in the surface activity and the resultant penetration of the fiber by the solution.

The indicated lack of efficiency of most penetration agents at elevated temperatures was checked in the following way:

Weighed skeins of cotton yarn were wet out at 93° C. by the method of Draves and Clarkson (*2*). The skeins were then subjected to the standard centrifugal procedure and it was shown that the average amount of water retained by the skeins was 82 per cent of the weight of the dry cotton. Further tests on this point were made by submerging weighed skeins of unbleached cotton yarn in boiling water for a period of 10 minutes. The skeins were removed and subjected to the standard centrifugal procedure. The amount of water retained by the skein was 90 per cent of the weight of the yarn.

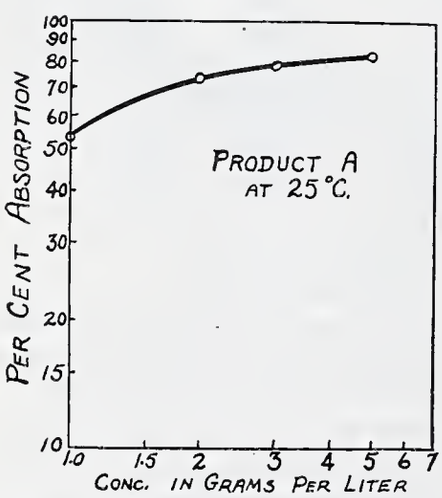

Figure 1. Penetration with Solutions of Product A in Water at 25° C.

These data add further proof that the lack of efficiency at elevated temperatures, observed in the solutions of the wetting-out agents, is not due to unexpected changes in the nature of the fiber or to a variable expulsion of the liquor at varying temperatures.

The ease of removal of the absorbed solution from yarn is obviously related to the viscosity of the solution. With the exception of soap solutions, the viscosities of the solutions of penetration assistants used in the experimental work reported in this paper are approximately that of water. It was observed from the data reported in Table III that the maximum apparent absorption of water by cotton yarn immersed in soap solutions is uniformly greater at the higher concentrations than the indicated absorption from the solutions of the other assistants. The following tests show that in general this apparent difference is due to a difference in the relative viscosity of the solutions: A stock solution of product B with gelatin was prepared, such that the solutions of product B and soap at 25° C. possessed the same relative viscosities at a concentration of 5 grams per liter of the assistant. Tests of the amount of solution retained by the yarn after being run through the standard centrifugal procedure were made over a range of concentrations. Comparisons of the quantity of solution retained by cotton yarn when immersed in solutions of product B, product B plus gelatin, and soap are made in Table IV.

Table IV. Relationship of Viscosity to Retention of Solution in Penetration Tests

Concn.	Product B	Product B + Gelatin	Soap
G./l.	%	%	%
1.0	69.1	68.5	66.4
2.0	81.2	84.1	79.5
3.0	83.6	88.5	85.2
5.0	81.5	87.5	94.1

The data in Table IV show that solutions prepared from the same assistant but with different viscosities at comparable concentrations differ appreciably from each other in the values which they give for retention of the solution.

While the apparent greater absorption of water from soap solutions is accounted for at most concentrations on the basis of the greater viscosity of the soap solutions, this explanation does not apply at a concentration of 5 grams per liter. The concentration of soap micelles on the cotton fiber might be advanced as an explanation. However, at concentrations below 1 per cent the soap micelles are very small and it is to be expected that they will not concentrate on the fiber to a greater extent than they are absorbed with the solution during a 15-second contact.

Penetration of Hard Water Solutions

One of the outstanding advantages of the various penetration assistants as compared with soap is the ability of solutions of the products to effect penetration in hard water solutions under conditions where soap is coagulated. Tests were made of the penetration efficiency of products A, B, and D in a solution containing 400 p. p. m. of calcium chloride. This concentration of calcium chloride is above the limit of the hardness of the water ordinarily encountered in industrial practice. A summary of the data obtained is given in Table V.

Table V. Solution Retained by Cotton Yarn at 25° C. from Solutions of Textile Assistants in Presence of Calcium Chloride (0.4 g./l.)

Concn.	Product A	Product B	Product D
G./l.	%	%	%
0.1	25.5	29.5	..
0.2	31.2	33.8	22.2
0.5	43.8	47.9	35.1
1.0	60.5	55.6	52.5
2.0	76.9	75.2	66.9
3.0	79.9	84.0	..
5.0	80.2	83.2	80.2
7.5	..	..	84.2
10.0	..	..	81.1

It is evident from a comparison of the data in Tables III and V that the efficiency of products A and D as penetration assistants is actually increased in calcium chloride solutions as compared with distilled water solutions. On the other hand the efficiency of solutions of product B decreases slightly under the same conditions. However, the general order of effectiveness remains product B > product A > product D.

Application to Wool and Silk

The centrifugal method has been applied in this laboratory for the evaluation of the effects obtained by the use of penetration assistants with wool and silk as well as with cotton. The wool skeins used in these tests were prepared from scoured wool yarn (30/2), while the skeins of silk were prepared from Spanish floss silk in the gum (2 ply). The tests were made in distilled water solution at 25° C. A comparison of the data obtained by immersing skeins of cotton, wool, and silk in the gum, in solutions of product B over a range of concentrations is given in Table VI.

Table VI. Water Absorbed by Cotton, Wool, and Silk from Solutions of Product B

Concn.	Cotton	Wool	Silk
G./l.	%	%	%
0.0	24.0	54.4	40.0
0.5	52.2	52.0	45.7
1.0	69.1	51.8	48.5
3.0	83.6	52.7	58.8

The maximum amount of water retained by unboiled-out cotton yarn has been shown to be 90 per cent. Wool yarn, after immersion for 180 seconds in a solution of product B of 5 grams per liter concentration, retains 56 per cent of its weight of moisture, while silk in the gum after immersion under similar conditions retains 77 per cent of its weight of water.

The tests summarized in Table VI show that well-scoured wool wets out readily in water. The results obtained with the silk in the gum are interesting since they show that while the rate of penetration is entirely different from that observed with cotton, a very definite effect can be evaluated by the centrifugal method.

Relationship of Surface Tension to Penetration of Textile Fibers

Measurements of the surface tension of solutions of several assistants were made over a range of concentrations in order to determine whether or not a definite relationship can be established between penetration and surface tension. The measurements were made with the du Noüy ring type of tensiometer. The instrument was calibrated against distilled water and the values given in Table VII are corrected on the basis of the calibration. The surface tensions of solutions of products A, B, C, and D, and soap at 25° C. are given. Each value given in the table represents an average of five experimental determinations.

Table VII. Surface Tensions of Solutions of Textile Assistants

Concn.	Product A	Product B	Product C	Product D	Soap
G./l.	*Dynes/cm.*	*Dynes/cm.*	*Dynes/cm.*	*Dynes/cm.*	*Dynes/cm.*
0.0	72.0	72.0	72.0	72.0	72.0
0.1	..	43.3	41.8	33.0	33.9
0.2	..	33.3	..	31.5	30.6
0.5	51.5	28.3	35.3	31.6	26.9
1.0	44.8	27.9	34.5	32.0	26.7
2.0	..	27.0	34.7	31.6	26.7
2.5	38.2	..	..	..	..
3.0	..	26.7	..	31.6	26.9
5.0	34.1	28.9	32.8	31.4	27.3
10.0	32.6	..	34.0	31.1	..

These data show that the presence of soap, product B, and product D produces marked lowering in the surface tension of water. While the surface tensions of product A solutions are relatively quite low, product A produces the least effect of the five assistants. These data show that while there is the expected general increase in penetration ability with a decrease in the surface tension there is no general quantitative relationship. For example, solutions of product A at a concentration of 5 grams per liter show a surface tension of 34.1 dynes per centimeter, a value which is higher than that found for solutions of product D or soap at a concentration of 0.1

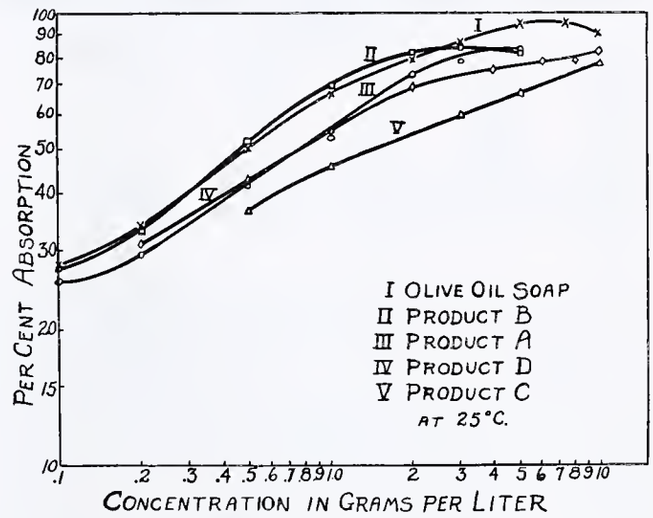

Figure 2. Water Absorbed by Cotton Yarn at 25° C. from Solutions of Textile Penetration Assistants

gram per liter. However, data obtained by the centrifugal method (Table III) show that cotton yarn absorbs 83 per cent of its weight of a solution containing 5 grams per liter of product A, while the quantity of liquid absorbed from a solution of soap at a concentration of 0.1 gram per liter is less than 28 per cent. It is evident from this and other comparisons which can be made from the data in Tables VII and III that there is no quantitative relationship between the surface tension of a solution of a textile assistant and its ability to penetrate textile fibers.

Critical Survey of Methods Based on Sinking Times

The most satisfactory sinking-time method is that of Draves and Clarkson (*2*). Data have been accumulated in this laboratory which make possible a comprehensive comparison between the sinking-time method as developed by Draves and Clarkson and the centrifugal method described in this paper.

The sinking-time method, as applied by Draves and Clarkson, measures the time required for an aqueous solution of the textile assistant to wet a submerged 5-gram skein of unbleached cotton yarn to an extent such that its weight plus the weight of absorbed liquid, together with that of an attached 1.5-gram sinker will overcome the buoyant force of the wetting solution and cause the skein with its attached weight to sink to the bottom of a cylindrical container. This method can give only a measure of the time required for a textile fiber to reach a certain unknown degree of saturation with a solution containing a known concentration of wetting assistant.

Tests made of the wetting-out efficiency at 25° C. of aqueous solutions of products A, B, and D, and soap by the sinking-time method are summarized in Table VIII, and a graphical representation of the data is given in Figure 4. Each value given in Table VIII represents an average of seven experimental determinations, made with skeins of raw cotton yarn (40/2).

An examination of the data in Table VIII and of the graphical representation in Figure 4 shows that the sinking-time

method appears to give uniformly good results with solutions of products B and A, but very erratic results with solutions of soap and of product D. Very definite experimental difficulties were encountered in observations of the wetting times of both the soap and the product D solutions and these difficulties are reflected in the data.

Table VIII. Wetting-Out Time of Solutions of Textile Assistants with Cotton Yarn by Sinking-Time Method

Concn.	Product A	Product B 25° C.	Product B 49° C.	Product D	Soap
G./l.	*Sec.*	*Sec.*	*Sec.*	*Sec.*	*Sec.*
1.0	..	35.0	31.5	..	..
1.5	86.0	23.6	15.3	..	43.2
2.0	32.9	15.8	9.3	41.7	33.8
2.5	20.9	..	..	..	25.6
3.0	14.0	11.1	6.2	..	15.6
3.5	..	..	..	25.9	..
4.0	7.4	7.9	5.0	28.4	7.1
5.0	4.9	7.3	..	27.1	5.9
7.5	..	..	..	21.0	4.6
10.0	..	..	..	17.1	..

Determinations by the same method relating to the wetting efficiency of product B at 49° C. are also included in Table VIII and show that solutions of product B are considerably more efficient at 49° C. than at 25° C. Table III shows that this result is in direct contradiction to that obtained with the centrifugal method. A contradiction of this nature is not unexpected, for the sinking-time method depends fundamentally upon the tension at the interface liquid–adsorbed gas. It is obvious that this tension is extremely sensitive to variations in temperature. On the other hand the centrifugal method depends basically upon the tension at the interface fiber-liquid and it is this interface that is of fundamental importance in the penetration of the fiber. The data in Tables III and VIII give additional proof that the quantitative evaluation of a penetration assistant by means of the sinking-time method alone may easily give misleading results and lead the investigator to erroneous conclusions. The centrifugal method of testing shows that solutions of soap are considerably superior to those of product A as penetrating agents in distilled water while the sinking-time method would indicate that solutions of soap are slightly inferior. This discrepancy probably lies in the difficulty of obtaining satisfactory determinations of the wetting-out times in soap solutions by the sinking-time method. The sinking-time method shows that concentrations of 2 grams per liter of product B and 12 grams per liter of product D in distilled water solution are required to produce wetting out of cotton yarn in a 15-second wetting time. This indicates that product B is six times as efficient as product D in producing this degree of effectiveness. On the other hand, according to the centrifugal method a concentration of 2.4 grams per liter of product B produces 82 per cent absorption in cotton yarn during an immersion time of 15 seconds, while a concentration of 10 grams per liter of product D is required to produce the same effect. Product B is only four times as effective as product D on this basis.

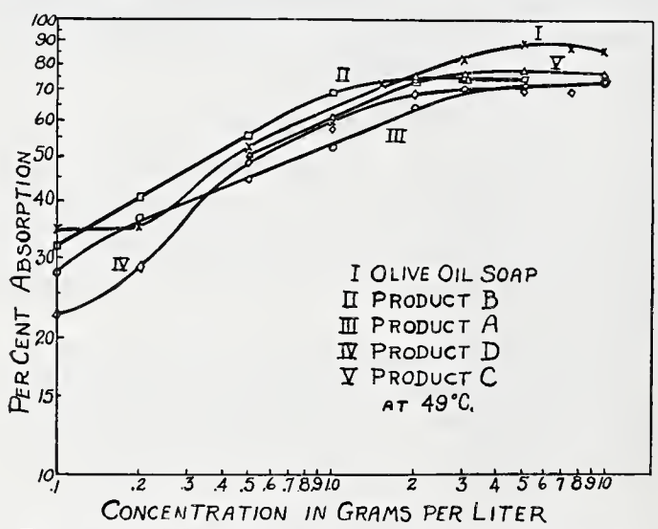

Figure 3. Water Absorbed by Cotton Yarn at 49° C. from Solutions of Textile Penetration Assistants

The sinking-time method for the evaluation of wetting agents is quite limited in the range of concentrations over which it may be employed. In the evaluation of agents with which this method has been successfully used the results are erratic when the actual time measured is greater than 40 to 50 seconds. Thus the lowest concentration of penetration assistant which can be evaluated is approximately 0.1 per cent or 1 gram per liter. However, with many agents of excellent wetting power the method breaks down when the concentration is from 2 to 3 grams per liter. The sinking-time test cannot be used for a quantitative comparison of the efficiencies of penetration assistants of different types or for the comparison of the relative efficiency at different temperatures. On the other hand the sinking-time method has been found to be decidedly valuable in the standardization of the alkylnaphthalenesulfonic acid type of penetration assistants. This is largely because slight changes in concentration cause relatively large variations in the sinking time as observed in a logarithmic plot of concentration against sinking time. As a result the actual strength of the wetting assistant present can be determined within an experimental error of 5 per cent even though the values for the sinking time may be in error by a considerably greater figure.

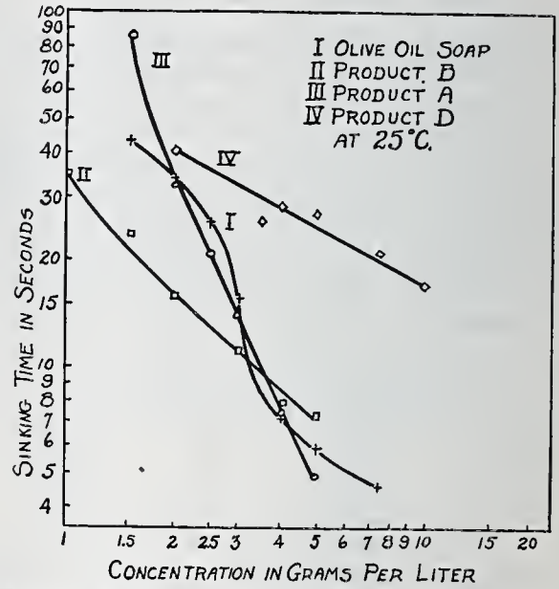

Figure 4. Wetting-Out Efficiency of Products A, B, and D, and Soap at 25° C.

Advantages of Centrifugal Method

The centrifugal method is of value for the comprehensive evaluation and comparison of textile assistants. Evaluations made by this method give a direct measure of the most important factor in the penetration of textile fibers—i. e., a measure of the quantity of a solution absorbed by the fiber. The amount of solution absorbed at the end of any time at any desired concentration of wetting agent can be determined regardless of the degree of saturation which the fiber has reached. The centrifugal method makes possible a determination of the maximum absorption of liquid by a fiber in solutions of all textile assistants. Measurements may be made at any temperature with the assurance that the results obtained are comparable with those obtained at any other temperature. The method can be applied to cotton, wool, or silk fibers.

The technic involved in the use of the centrifugal method

can be readily mastered by any person experienced in laboratory methods. The time required for a test compares favorably with the sinking-time method. A series of five individual determinations, required for the determination of the efficiency at a given concentration, may be made in 15 to 20 minutes, depending naturally upon the length of the actual sinking-time observed.

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Antimony as an Indicator Electrode in Potentiometric Titration of Iron and Aluminum

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The antimony electrode is applied as indicator electrode to the direct titration of ferric chloride and aluminum chloride with sodium hydroxide solution. Data are given which show the general suitability of the antimony electrode for the titration of aluminum and iron chlorides. The method also affords an approximate analysis of mixtures of the two salts.

Antimony has been found by many investigators to be well adapted as an indicator electrode to the potentiometric titrations of acids and bases and to the determination of the pH of various solutions. The antimony electrode has also found application in a number of titrations involving precipitation reactions.

In the titration of aluminum and magnesium chlorides with sodium hydroxide solution, Treadwell and Bernasconi (*3*) have found that in the titration of aluminum chloride two jumps in the antimony electrode potential occur, one when the aluminum hydroxide has been quantitatively precipitated, and one, which is less pronounced, when the aluminate has been produced. In the titration of mixtures of aluminum and magnesium chlorides with sodium hydroxide, jumps in the electrode potential occur at the precipitation of aluminum and magnesium hydroxides, respectively, the second jump being too early, causing an error of from 1 to 2 per cent.

The antimony electrode has been found by Malvea and Withrow (*2*) to be satisfactory to indicate the end points in the titration of mixtures of calcium and magnesium with sodium hydroxide solution.

An abnormal titration curve occurs, according to Elder (*1*), for the antimony electrode in acid solutions of ferric chloride, probably because of the presence of pentavalent antimony in solution.

The purpose of this investigation is to show the application of antimony as an indicator electrode in the precipitation of ferric iron and aluminum from neutral solutions of their chlorides by the addition of sodium hydroxide solutions.

Procedure

The titrations were carried out using antimony as the indicator electrode. The electrode was prepared from electrolytically refined antimony by casting in a carbon mold, and undoubtedly contained some oxide; however, no precaution was taken to exclude the oxide from the cast metallic rod. The electrode had a length of 4.5 inches (11.25 cm.) and a diameter of 0.25 inch (0.63 cm.). In all the titrations the potential of the indicator electrode was measured against the saturated calomel electrode. The titration vessel consisted of an open 400-cc. beaker. The potential of the electrode combination was measured by means of a students' type Leeds and Northrup potentiometer, No. 7651, in conjunction with a Leeds and Northrup galvanometer No. 2310. In all cases, unless otherwise indicated, the solutions were kept continually agitated by means of a current of air bubbling through the solution in the titration vessel. All experiments were carried out at room temperature, which varied from 24° to 28° C.

Three stock solutions of ferric and aluminum chloride were prepared having the following normalities with respect to iron and aluminum: ferric chloride, 0.3146 *N*, 0.9969 *N*, and 0.1000 *N*; aluminum chloride, 0.2968 *N*, 1.0045 *N*, and 0.1000 *N*. The aluminum chloride solutions were standardized gravimetrically and the ferric chloride solutions by reduction with stannous chloride and titration with potassium bichromate solution. A determination of the chloride content of the ferric and aluminum chlorides used in preparing the stock solutions indicated that the error encountered in the calculation of the theoretical quantity of the sodium hydroxide solutions required for the samples of ferric and aluminum chlorides titrated was of little consequence, since the commercial preparations of ferric and aluminum chlorides used contained an undeterminable amount of basic salts.

Titrations of various quantities of ferric and aluminum chlorides, both separately and as mixtures, were carried out using sodium hydroxide solutions approximately 1 *N*, 0.5 *N*, and 0.1 *N*. These solutions were prepared from carbonate-free sodium hydroxide and carbon dioxide-free water and were standardized against pure recrystallized succinic acid, using phenolphthalein as indicator. The strengths of the various sodium hydroxide solutions are shown in the tables.

Three series of experiments were carried out, involving sodium hydroxide solution approximately 0.5 *N*, and 1 *N*, and 0.1 *N*, respectively. In the first series the effect of the presence of sodium and ammonium sulfate was also determined.

Because of the difference in solubilities of ferric and aluminum hydroxide, the ferric hydroxide was found to be quantitatively precipitated first, giving rise to a jump in the potential of the antimony electrode at the iron equivalence point.

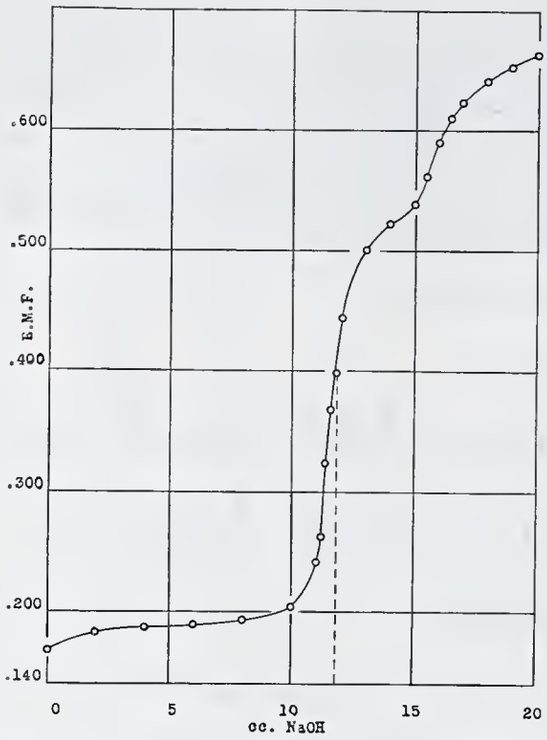

FIGURE 1. E. M. F.–VOLUME CURVE FOR TITRATION OF ALUMINUM CHLORIDE WITH SODIUM HYDROXIDE SOLUTION (EXPERIMENT 3, TABLE I)

The precipitation of the aluminum hydroxide followed and the second jump in the potential appeared at the quantitative formation of aluminum hydroxide. In the case of the titration of aluminum chloride alone, two jumps in the potential appeared, as found by Treadwell and Bernasconi, one when aluminum hydroxide was quantitatively precipitated, and a second less pronounced jump when the aluminate was produced. The second jump appeared to be rather indistinct and unsuitable for accurate determinations. In the case of the titration of ferric chloride alone, only one jump in the potential occurred, the one at the quantitative precipitation of ferric hydroxide.

TABLE I. SERIES 1 OF TITRATIONS

Expt.	Vol. of Soln.	Present FeCl3	Present AlCl3	Vol. of NaOH[a] Theoretically Required FeCl3	Vol. of NaOH[a] Theoretically Required AlCl3	Vol. of NaOH[a] Actually Used FeCl3	Vol. of NaOH[a] Actually Used AlCl3	Error FeCl3	Error AlCl3
	Cc.	*Grams*	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
1	50	0	0.3297	0	11.78	0	11.80	....	+0.17
2	75	0	0.3297	0	11.78	0	11.70	....	−0.68
3	125	0	0.3297	0	11.78	0	11.80	....	+0.17
4	50	0.4250	0	12.49	0	12.40	0	−0.72	....
5	75	0.4250	0	12.49	0	12.50	0	+0.08	....
6	125	0.4250	0	12.49	0	12.40	0	−0.72	....
7	150	0.4250	0.3297	12.49	11.78	12.40	11.80	−0.72	+0.17
8	150	0.8500	0.3297	24.98	11.78	24.98	11.90	0.00	+1.02
9	150	0.4250	0.6594	12.49	23.56	11.90	24.00	−4.72	+1.87
10[b]	150	0.4250	0.6594	12.49	23.56	11.80	23.40	−5.52	−0.67
11[c,d]	125	0	1.8275	0	27.00	0	26.60	....	−1.48
12[e]	125	0	1.8275	0	27.00	0	26.60	....	−1.48
13[c]	125	1.3519	0	28.60	0	29.00	0	+1.39	....
14[c]	125	0.6759	0.9137	14.20	13.50	13.00	15.00	−8.45	+11.11
15[f]	125	0.6759	0.9137	14.20	13.50	12.80	13.40	−9.85	−0.74

[a] 0.6297 *N* NaOH used.
[b] 25 cc. of 15 per cent NH_4Cl solution added.
[c] 2 grams of Na_2SO_4 added.
[d] In experiments 11 to 15, inclusive, 0.5059 *N* NaOH was used.
[e] 1 gram of Na_2SO_4 added.
[f] 2 grams of $(NH_4)_2SO_4$ added.

In order to determine the end point of each reaction, curves were constructed with e. m. f. of the electrode combination plotted as ordinates and volume of sodium hydroxide solution as abscissas. The definite location of the point of maximum increase in potential was determined from these curves by means of the oscillatory tangent to the curve and also from differential curves in which the volume of sodium hydroxide solution was plotted against the change of potential with unit change of volume of sodium hydroxide ($\Delta E/\Delta V$).

Curves for the titrations in this first series of experiments, which are typical of the curves in all the titrations in this investigation, are shown in Figures 1, 2, 3, and 4. The determination of the end points is shown and it is seen that the accuracy of the end point is largely dependent upon the correct interpretation of the curve. The differential curve gives a much more definite determination of the end points, since it brings out more clearly the points of maximum increase in potential of the indicator electrode.

TABLE II. SERIES 2 OF TITRATIONS

Expt.	Present[a] FeCl3	Present[a] AlCl3	Vol. of NaOH[b] Theoretically Required FeCl3	Vol. of NaOH[b] Theoretically Required AlCl3	Vol. of NaOH[b] Actually Used FeCl3	Vol. of NaOH[b] Actually Used AlCl3	Error FeCl3	Error AlCl3
	Grams	*Grams*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
16	0.5390	0.4460	11.10	11.19	11.20	11.20	+0.90	+0.08
17	1.0780	0.4460	22.20	11.19	21.60	11.40	−2.70	+1.84
18	0.5390	0.8920	11.10	22.38	11.00	22.50	−0.90	+0.52
19[c]	1.0780	0.8920	22.20	22.38	21.60	22.70	−2.70	+1.41
20	0.2695	1.1150	4.52	22.80	4.40	22.40	−2.70	+2.23
21	1.3475	0.2230	22.62	4.56	22.50	5.00	−0.55	+9.67
22[d]	0.5390	0.4460	9.05	9.12	10.30	11.30	−13.80	+23.90

[a] In all cases volume of titration solution was 100 cc. at the start.
[b] 0.8972 *N* NaOH used.
[c] In experiments 19 to 21, inclusive, 1.1012 *N* NaOH was used.
[d] Hydrogen electrode used.

TABLE III. SERIES 3 OF TITRATIONS

Expt.	Present[a] FeCl3	Present[a] AlCl3	Vol. of NaOH[b] Theoretically Required FeCl3	Vol. of NaOH[b] Theoretically Required AlCl3	Vol. of NaOH[b] Actually Used FeCl3	Vol. of NaOH[b] Actually Used AlCl3	Error FeCl3	Error AlCl3
	Gram	*Gram*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%	%
23	0.0540	0.0444	10.00	10.00	10.10	10.10	+1.00	+1.00
24	0.0270	0.1111	5.00	25.00	4.80	25.20	−4.00	+0.80
25	0.1352	0.0222	25.00	5.00	26.00	5.30	+4.00	+6.00
26[c]	0.1081	0.0889	20.00	20.00	19.90	20.20	−0.50	+1.00
27[d]	0.1081	0.0889	20.00	20.00	19.80	20.70	−1.00	+3.50

[a] Volume of solution at start of titration, 100 cc.
[b] 0.1 *N* NaOH used.
[c] Agitated with a stream of hydrogen bubbling through solution.
[d] Hydrogen electrode used in this experiment.

In the second series of experiments the titrations were made with sodium hydroxide of approximately normal strength. More ferric and aluminum chlorides were present than in the first series of experiments. In this series of titrations, various mixtures of ferric and aluminum chloride were used, and the data in Table II show the results obtained.

The third series of experiments was carried out with 0.10 *N* sodium hydroxide solution and more dilute solutions of ferric and aluminum chlorides. As in the second series, one titration was made using the hydrogen electrode in order to make a comparison with the antimony electrode. Table III gives the data for the titrations in series 3.

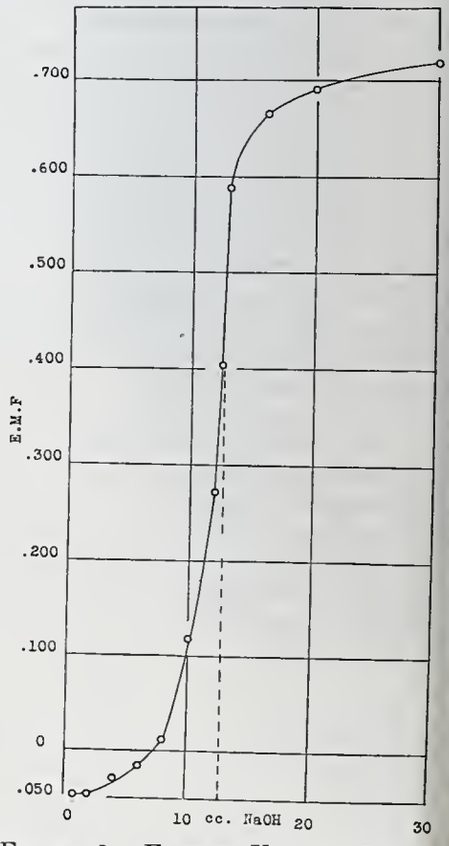

FIGURE 2. E. M. F.–VOLUME CURVE FOR TITRATION OF FERRIC CHLORIDE WITH SODIUM HYDROXIDE SOLUTION (EXPERIMENT 6, TABLE I)

Results

The data given in the tables indicate that antimony is suitable as an indicator electrode in the potentiometric titration of either aluminum or ferric chloride with sodium hydroxide solution. The end point is clearly defined and accurately located by the jump in the electrode potential at the quantitative precipitation of the hydroxides. The slight jump in

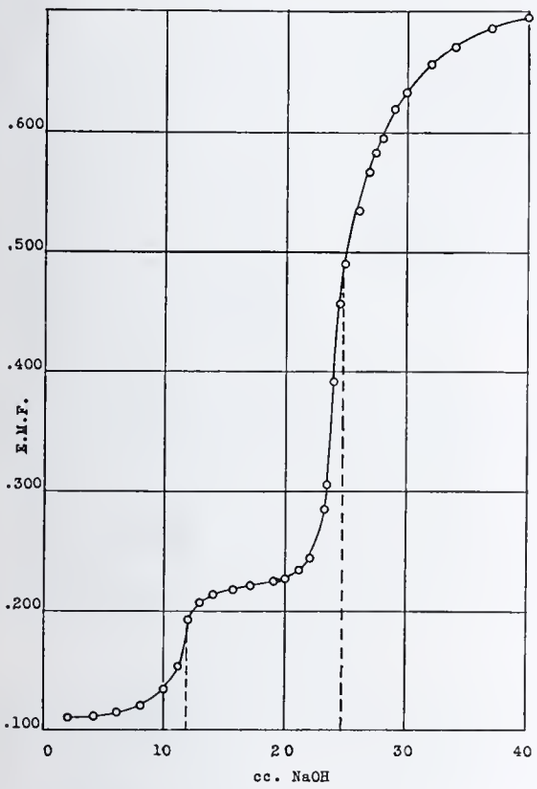

Figure 3. E. m. f.–Volume Curve for Titration of Mixture of Aluminum and Ferric Chloride with Sodium Hydroxide Solution (Experiment 7, Table I)

potential (Figure 1) at the equivalence point for the aluminate formation is less distinct and practically imperceptible in the case of mixtures of aluminum and ferric chlorides and is not satisfactory, under the conditions of these experiments, for the determination of the end point. Dilution seems to have little effect upon the accuracy of the method.

In general it was found that in the titrations involving mixtures of aluminum and ferric chlorides, the end point indicating the equivalence point for ferric hydroxide was too early and the end point for aluminum hydroxide too late. In all cases the jump in the electrode potential at the ferric hydroxide equivalence point was less pronounced.

The potentiometric titration of mixtures of ferric and aluminum chlorides with sodium hydroxide, using an antimony indicator electrode, affords a method for an approximate analysis. Titration errors occur which prohibit a more accurate analysis. The accuracy is greater when nearly equal proportions of the two salts are titrated, probably because the titration curves can be more easily interpreted. The accuracy is no doubt impaired by the formation of basic salts at the location of the jump in potential, since no precautions were taken to prevent this difficulty at the end point. Evidence of the formation of basic salts is clearly indicated by the small jump in potential immediately before the aluminum end point in Figure 4.

The presence of sodium sulfate in the solutions of either aluminum or ferric chloride caused an increased error, as is seen from Table I. In the case of mixtures of aluminum and ferric chlorides, the presence of sodium sulfate caused errors of from 8 to 11 per cent, making the method prohibitive in the presence of this alkali sulfate. The presence of ammonium sulfate had an effect similar to that of sodium sulfate. Normal titration curves were obtained in the experiments in which sodium and aluminum sulfate was added.

The strength of the sodium hydroxide solution used for the titrations and the amounts of ferric and aluminum chlorides present in the solutions to be titrated seem to have, in general, little effect on the suitability of antimony as the indicator electrode (Table I).

The hydrogen electrode was found to be inferior to the antimony electrode for the direct titration of iron and aluminum by sodium hydroxide, especially in concentrated solutions, probably because the platinized surface is poisoned by the salts in solution. In more dilute solutions, the hydrogen electrode behaves in the same manner as the antimony electrode but exhibits no advantages.

Stirring by means of air was found to be a suitable method of causing agitation during the titrations. There was no perceptible difference in the action of the antimony electrode where hydrogen was used in place of air.

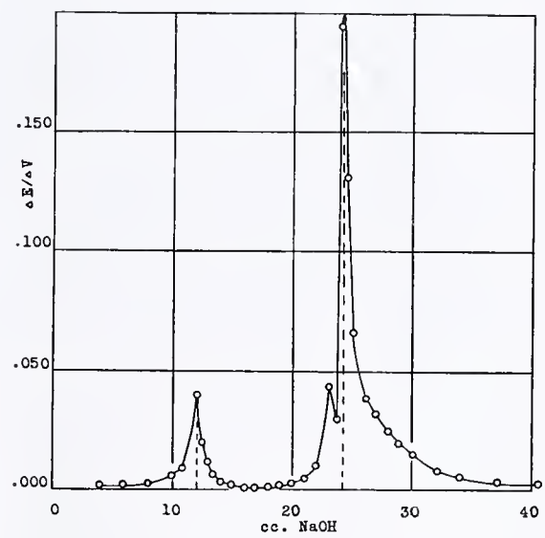

Figure 4. Differential Curve for Titration in Figure 3

The potential of the antimony electrode reached equilibrium rapidly, except at the very start of the titrations. The presence of a relatively large quantity of iron in the solution seemed to affect the electrode, causing it to be covered with a dark coating. When most of the iron had been precipitated, the dark coating disappeared and the potential of the electrode thereafter reached equilibrium almost immediately after the successive additions of sodium hydroxide solution. In contrast to this, when the hydrogen electrode was used equilibrium was reached only after 10 to 15 minutes throughout the entire titration. This fact, together with the other factors above mentioned, points favorably to the use of the antimony electrode for the titration of ferric and aluminum chlorides with sodium hydroxide.

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ter Meulen Method for Direct Determination of Oxygen in Organic Compounds

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The method of ter Meulen for the direct determination of oxygen in organic substances containing carbon, hydrogen, and oxygen has been examined. Very satisfactory results can be obtained if certain modifications are made. These involve primarily the use of a furnace to volatilize the sample, the use of platinum-coated granular quartz as a cracking surface, and the use of a very active, thoria-promoted, nickel catalyst.

Although methods for the direct determination of oxygen in organic compounds have been studied for over eighty years, it is probable that oxygen is still most frequently determined by difference. The defects of the indirect method are obvious in that it is time-consuming and subject to accumulated errors, if not gross error—e. g., where complete combustion is difficult. The need of a rather simple, reliable, direct method is apparent. Among the methods proposed during the past decade (*1–3, 6–10*) for the direct determination of oxygen in organic combination, that of Meulen stands out prominently. Although this method gave excellent results in the hands of its originator, and was found by Schuster (*15*) to give accurate results with benzoic acid, but not with pure coal, Dolch and Will (*2*), who studied the method in considerable detail, were unable to obtain satisfactory results even with such a simple substance as crystallized oxalic acid. Furthermore, students of advanced analytical chemistry have been unable to obtain anything like the accuracy claimed for the method. It was therefore considered desirable to investigate this method. Briefly it consists in vaporizing the sample in a stream of hydrogen which flows over a red hot surface where the organic substance is decomposed, forming oxides of carbon, water, and gaseous hydrocarbons. The gases then pass over a nickel catalyst where the oxides of carbon are converted to methane and water. Provision is made for evaluating water and any carbon dioxide in the exit gases, thus giving data for the calculation of the oxygen present. In the present work certain modifications of this method have been found desirable in order to obtain consistently good results.

Vaporization of Sample

As Meulen points out (*9*), the success of the method depends largely upon vaporizing the sample very slowly and uniformly. This necessitates very careful manipulation with a microburner for a half hour or more. If the sample is heated in an electric furnace, however, it may be easily vaporized at the desired rate and a tedious and uncertain operation avoided. While the temperature to be employed in the furnace varies with the substance undergoing analysis, it is usually best to heat rapidly to the melting point of the substance and then to raise the temperature just fast enough to avoid any appreciable condensation of water in the side arm of the first calcium chloride tube. Too rapid heating causes poor results because of incomplete methanation, sublimation of the sample through the absorption train, etc. While with substances like β-naphthol especial care is necessary in order to avoid sublimation, in most cases 20 to 30 minutes suffice to vaporize 200 to 300 mg. of sample.

The Cracking Surface

Various hot "cracking" surfaces have been proposed by Meulen (*6, 7, 9*), such as fine nickel wire, platinized asbestos, and pure asbestos. The authors' experience with iron or nickel was unsatisfactory and they have found it extremely undesirable to have asbestos present anywhere in the system because of the slowness with which it gives up water. Inasmuch as the analysis depends primarily upon the amount of water formed, it is obvious that any uncertainty about sources of water easily vitiates the results. A very satisfactory cracking surface can be made by igniting 20-mesh granulated quartz with about one-twentieth the amount of ammonium chloride and enough 10 per cent platinum chloride solution to wet the mass. The mass is heated in a casserole to dull redness long enough to decompose the ammonium platinic chloride and to volatilize completely the excess ammonium salts. The result is a light gray mass of platinum-coated quartz granules which is employed at red heat.

The Catalyst

As no provision is made for the evaluation of carbon monoxide in the exit gases, it is essential to have a very active hydrogenation catalyst. It is probable that the difficulties of Dolch and Will (*2*) were in part due to an inactive catalyst although they used the asbestos-supported nickel recommended by Meulen. Very active methanation catalysts (*5, 14*) can be prepared by using thoria as a promoter for nickel. Rugged catalysts of high activity were prepared in the present work by dissolving pure thorium nitrate in pure nickel nitrate melted in its water of crystallization, in amounts necessary to give 2 per cent thorium oxide on the nickel present. The mass was stirred continuously, while igniting over a Bunsen burner, to a fine gray powder. To insure complete destruction of the nitrates, the mass may well be cooled and finely ground once during the ignition. Because the thoria acts also as a support, the oxide may be reduced with hydrogen at 350° and finally at 400° C. While the initial reduction required, to give a blank of about 1 mg. of water per hour at the rates of hydrogen flow used, occupied 2 to 3 days, subsequent reductions could be carried out overnight at 400° C. To avoid delays extra catalysts may be reduced independently and sealed off in glass tubes in an atmosphere of hydrogen. Such catalysts may be transferred to the analysis system with only superficial oxidation if a rapid stream of hydrogen is issuing from it. Thoria-promoted catalysts are pyrophoric and so become incandescent when air is drawn through the analysis tube, as is necessary when carbon deposited on the cracking surface must be burned off. With continued use they become less active and may then be heated slightly during the burning-out process in order to remove any deposited carbon or volatile poisons. If the samples analyzed contain no catalyst poisons, such as mercury, sulfur, halogens, etc., one charge of 5 to 10 grams of catalyst may serve for 10 to 15 analyses before requiring reactivation. Substances such as anthraquinone, which clog by depositing much carbon on the first portions of the platinized quartz, necessitate burning out carbon after 4 to 5 analyses.

In order to have a quantitative removal of the oxides of carbon, it is essential that conditions be such that the following reactions go very near completion:

$$CO + 3H_2 = CH_4 + H_2O$$
$$2CO + 2H_2 = CO_2 + CH_4$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

While there is evidence that the equilibrium constants for these reactions reach a maximum between 300° and 400° C., other reactions probably intrude and complete equilibrium data (*4*, *11*, *12*) in this temperature region are not available. The temperature range of 350° to 420° C. proposed by Meulen seems unnecessarily high and 300° to 350° C. has proved satisfactory with the active catalysts used here. Using a large excess of hydrogen the authors have found 350° C. to be the most generally applicable temperature because of the faster rate of reaction. The relatively high rate of hydrogen flow employed in the present work—90 cc. per minute—is advantageous too because it tends to prevent the deposition of carbon (*13*) on the catalyst, and also shortens the time of analysis by allowing the system to be rapidly swept out at the end.

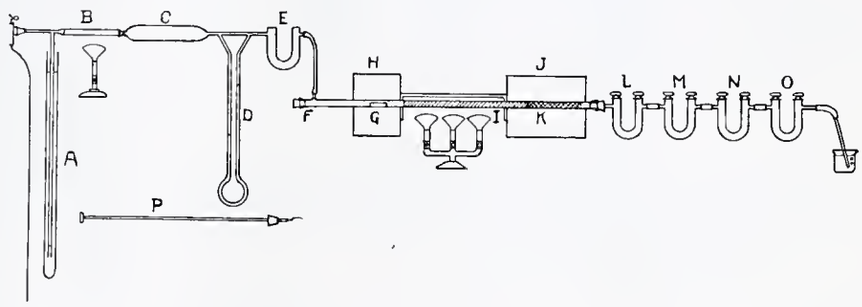

Figure 1. Diagram of Apparatus

The Apparatus

A quartz tube is an indispensable part of the apparatus shown in Figure 1. It should be about 1 meter long, about 1 cm. in inside diameter, and preferably provided with a small side arm which greatly facilitates the safe introduction of the sample. If desired, the plain tube suggested by Meulen (*9*) may be used. While it is desirable to have at least the portion of the tube which holds the sample boat made of transparent quartz, the whole tube may be of opaque material if the platinum boat *G* is provided with an eyelet into which the hook of the loading rod *P* fits, so that the sample cannot be overturned when inserted. The substitution of an opaque quartz tube removes the only expensive part of the apparatus. About 5 cm. from the exit end of the tube *F* a plug of glass wool is inserted, followed by 5 to 10 grams of the prepared oxides *K*. A perforated platinum disk is slipped in and then enough of the platinized quartz *I* to fill the tube about two-thirds full. Another perforated platinum disk may now be inserted if desired, but the tube must not be packed too tightly. The filled tube is conveniently placed in an ordinary organic combustion set-up in which the smallest furnace, *H*, is used to volatilize the sample, and the medium-sized unit, *J*, to heat the catalyst. The largest furnace may be used to heat the granulated quartz to redness but this may be conveniently and efficiently done, as has been the practice in most of the present work, by using the full temperature of 3 ordinary Bunsen burners. In the latter case, 2 shields and a light covering of asbestos paper are sufficient to retain the heat. The ends of the tube *F* are flared out to receive rubber stoppers snugly. The U-tubes *L* and *M* contain calcium chloride, and *N* contains ascarite and calcium chloride, while *O* is a calcium chloride guard tube. Electrolytic hydrogen is freed from oxygen by passing over hot palladized asbestos in *B*, dried over calcium chloride in *C*, measured in the flowmeter *D*, and finally dried over calcium chloride in *E*.

The Method

Having in the system a reduced catalyst, its temperature is brought to 400° C. and a rapid stream of hydrogen is passed for at least a half-hour interval. This is necessary even though the system is always kept under a positive pressure of hydrogen when not in use. During this interval the granulated quartz should be at full heat and the U-tubes may well be in place in order to flush them with hydrogen. The catalyst temperature is then lowered to just 350° C. and the recently weighed tubes *L*, *M*, and *N* are placed in the train. Hydrogen is passed at 90 cc. per minute for half an hour in order to obtain the blank which is by no means negligible. Since results are desired to 0.1 mg., the blank must be carefully determined—e. g., temperature and rate of hydrogen flow kept constant, and in case of doubt another should be taken after the analysis. Having ascertained the blank, the U-tubes are again attached but not opened. The hydrogen tank valve is opened so that 100 to 150 cc. per minute pass out through *A* and the weighed sample quickly inserted in *F*. Having placed the sample about 5 cm. from the hot cracking surface by means of the rod *P*, the solid rubber stopper is tightly replaced. The U-tubes are now opened, the hydrogen rate is adjusted to 90 cc. per minute, and *H* rapidly raised to the desired temperature. The sample is slowly and uniformly volatilized during the course of half an hour and then the temperature of *H* raised to 300° to 400° C. The furnace is then slid back and the tube holding the sample boat heated with the full heat of a blow torch. Strong heating is especially necessary with substances like sugars which leave a voluminous carbon in the boat. The greater portion of the second half hour is allotted to sweeping out the system. Thus the analysis proper usually takes an hour. One analysis can be immediately followed by another, with occasional blanks, until the tube becomes choked with carbon. With an active catalyst and following the above procedure, all the oxygen will be found as water in the first calcium chloride tube. The tubes *M* and *N* are therefore useful mainly as guard tubes. When it becomes necessary to remove the carbon from *I*, the quartz tube *F* is evacuated on a good water pump and air drawn over the hot quartz. When this operation is complete, the air is evacuated and replaced by hydrogen which starts reduction of the catalyst again. This procedure avoids the use of an inert gas like carbon dioxide and also does not disturb the set-up. Directions have been given in some detail in order to avoid ambiguity (*2*).

Results

The results of analyses made upon high-grade organic chemicals by the modified Meulen method are given in Table I. These results were obtained using an ordinary analytical balance and it is felt that by the use of semi-microtechnic somewhat better accuracy could be obtained, or smaller samples might be satisfactorily employed. The analyses made substantiate the soundness of the basic principles of the Meulen method for representative substances containing only carbon, hydrogen, and oxygen. While Meulen gives procedures by which materials containing also nitrogen, sulfur, chlorine, bromine, and iodine (*7*) can be handled, such substances have not been dealt with in the present work. It is hoped to report on these at a later date.

Table I. Results of Analyses by Modified Meulen Method

Substance	Weight of Sample	Temperature of Catalyst	Oxygen Found	Oxygen Calculated
	Gram	° *C.*	%	%
Succinic acid	0.1289	300	54.22	54.21
	0.1621	300	54.24	
	0.1830	350	54.26	
	0.1480	380	54.14	
Oxalic acid	0.1940	325	76.15	76.16
	0.1053	350	76.24	
Dextrose[a]	0.2566	300	53.39	53.31
	0.1293	350	53.30	
Cane sugar	0.2855	300	51.59	51.44
Benzoic acid[b]	0.2650	325	26.31	26.22
	0.2315	350	26.24	
Anthraquinone	0.2716	350	15.50	15.38
	0.2108	350	15.38	
Quinhydrone	0.1601	350	29.57	29.35
	0.1906	350	29.18	
β-Naphthol	0.2108	350	11.04	11.11
	0.2029	350	11.21	

[a] Bureau of Standards sample 41.
[b] Bureau of Standards sample 39c.

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Volumetric Determination of Small Quantities of Inorganic Iodine

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Recent attempts to increase the accuracy of the determination of iodine in biological material have been largely directed toward improvements in the procedure for destruction of organic matter. Though most methods described have employed the Winkler procedure (*25*) for the final estimation of the iodine, little attention has been given to the investigation of the accuracy of the procedure when applied to the small quantities of iodine dealt with in biological material. Recently several investigators (*2*, *17*) have held this procedure to be defective because of the risk of decomposition of iodides in acid solution. It is the purpose of this contribution, first, to show that under conditions to be described the estimation of small amounts of iodine, 1 mg. or less, by the Winkler procedure is both accurate and trustworthy; second, to report a study of the interference by other substances; and third, to make a practical application—namely, the determination of iodine in iodized salt.

Reagents and Apparatus

Standard Iodate Solution. An exactly 0.1 *N* iodate solution was prepared according to the directions of Jamieson (*9*), using Kahlbaum's purest potassium iodate. The solution so obtained was further diluted to give an exactly 0.005 *N* reagent.

Thiosulfate. Thiosulfate solutions 0.005 *N* seemed to be more stable if they contained 3.8 grams of crystallized borax ($Na_2B_4O_7.10H_2O$) per liter (*15*). The solution was standardized immediately before use, employing the optimum concentrations of acid and potassium iodide mentioned below.

Standard Potassium Iodide Solution. The iodine content of a specimen of potassium iodide was accurately determined by precipitation with silver nitrate, using the precautions recommended by Hillebrand and Lundell (*7*). The requisite amount of the salt was dissolved in water to give a solution so dilute that small quantities of iodine could be measured with sufficient accuracy.

Bromine. Iodine-free bromine was prepared by repeated washings of the c. p. product with water in the manner suggested by Karns and Donaldson (*11*). Early in the work it was found that the use of bromine water for oxidation purposes was inadvisable. Therefore, the following procedure, slightly modified from Schockaert and Foster (*22*), was employed: Bromine vapor, obtained by blowing air (washed with water and dried by calcium chloride) through a gas-washing tube containing bromine, was delivered just above the surface of liquid in a flask. Upon swirling the contents of the flask, sufficient bromine was dissolved to give a yellow color to the liquid. To prevent the expulsion of too large quantities of bromine it is wise to draw out to a capillary both the inlet and outlet tubes of the gas-washing tube.

Starch Indicator. This reagent containing salicylic acid for a preservative as recommended by Nichols (*19*) was found to be very satisfactory as to sensitivity and keeping qualities. A solution kept at room temperature with no aseptic precautions for over 6 months showed no deterioration in quality.

Other Reagents and Apparatus. Iodine-free water was produced by redistilling water from an alkaline permanganate solution. Pumice stone used for the prevention of bumping was prepared by boiling millimeter cubes in dilute nitric acid and, after washing thoroughly with water, igniting to a bright red heat in a porcelain crucible. All volumetric glassware was carefully calibrated. Titrations were carried out with 1-, 5-, and 10-ml. microburets.

Sensitivity of End Point

In order to gage the accuracy of a volumetric method, it is essential to know the sensitivity of the end point. Accordingly, experiments were carried out to ascertain the smallest quantity of iodine necessary to give a perceptible blue color to a solution 50 ml. of which contained 0.1 gram of potassium iodide, 1 ml. of 2 *N* sulfuric acid, and 1 ml. of starch indicator. Potassium iodate (0.001 *N*) was added from a micropipet in successive 0.002-ml. portions to the first appearance of a blue color. At 31° C. (room temperature in Baltimore in the summer of 1932), the following amounts of iodate iodine were necessary: 1 ml. volume, 0.08 γ; 10 ml.

volume, 0.5 γ; 100 ml. volume, 4 γ (1 γ = 0.001 mg.) Six times this amount of free iodine would be necessary for the production of a blue color, but the authors have chosen to express the results in terms of iodate iodine in order to define the sensitivity in terms of the amount of iodine present in the original material under analysis. The Erlenmeyer flasks employed for the experiments were respectively 25, 50, and 200 ml. At a temperature of 17° C., only 2 γ iodine was necessary to impart a blue color to 100 ml. of solution—that is, half the quantity required at 31° C. Therefore, the temperatures at which the thiosulfate solution is standardized and the actual determination is made should be approximately the same. Since completing this work a paper has appeared by Allott, Dauphinee, and Hurtley (*1*) reporting values very similar to those given here, though the authors fail to state the temperature in their experiments.

Since the sensitivity of the starch indicator when the total volume is 1 ml. is 0.08 γ of iodate iodine at 31° C., the determination at this temperature of quantities of iodine less than 8 γ would theoretically be subject to errors greater than 1 per cent. The authors have therefore confined their attention in this paper to quantities no smaller than 20 γ. It would appear that the titration of quantities of iodine smaller than this can be carried out more accurately at low temperatures where the sensitivity of the starch indicator is increased.

Effect of Acidity and Iodide Concentration

Acid solutions of iodides decompose with greater or less rapidity according to their H^+ concentration to liberate free iodine. Upon this fact—namely, the oxidation of hydriodic acid by atmospheric oxygen—are based the objections to the titrimetric method for iodine determination. Since the reaction (formulistically)

$$H^+ + I^- \rightleftharpoons HI \qquad (1)$$

is reversible, it should be possible to have a minimum of hydriodic acid formed if both the acid and iodide concentrations are as low as possible. On the other hand, the solution should possess the requisite acidity and iodide content for the reaction

$$IO_3^- + 5\,I^- + 6\,H^+ \rightleftharpoons 3\,I_2 + 3\,H_2O \qquad (2)$$

to go to completion.

If the titration were carried out under an inert gas such as nitrogen or carbon dioxide, there should be no appreciable oxidation of hydriodic acid and the acid concentration could be neglected. This procedure, however, is burdensome in routine laboratory work, so efforts were made to determine the effect of acid and iodide concentrations on titrations carried out in the presence of atmospheric oxygen.

Consideration of the effect of pH on the titration of free iodine with thiosulfate at the acid concentrations to be employed can be neglected, since Reith (*20*) has shown that the reaction is quantitative at pH values below 6.

It was found that variation of the iodide concentration within certain limits did not markedly affect the procedure. Optimum conditions were obtained when 0.1 gram of potassium iodide was present in 50 ml. of solution.

The effect of acidity, however, was more striking. It can be seen from the data given in the third column of Table I that the acid normality of the solution must be 0.02 or higher in order to carry Reaction 2 rapidly to completion. In the presence of air there is a marked increase in titer as the acid strength becomes greater than 0.1 *N*. This increase is presumably due to the oxidation by air of the larger amount of hydriodic acid formed according to Equation 1, since no such increase is noted in the absence of oxygen (column 4). Therefore, if the titration of small quantities of iodine is to be made in the presence of air, the pH of the solution must be between 1.0 and 2.0 if serious errors are to be avoided. Solutions of potassium iodide with a pH between 1.0 and 2.0 show no appreciable oxidation by air even after standing 0.5 hour. The rate of air oxidation appears to decrease with temperature. It is therefore possible that titrations could be carried out in higher acid concentrations than those recommended here if lower temperatures were employed.

Table I. Effect of Acidity

(5 ml. of 0.005 *N* KIO_3 titrated with $Na_2S_2O_3$. 0.1 gram of KI present, total volume 50 ml. Room temperature 20° ± 2° C.)

Experiment	Acid Normality	Thiosulfate Titer: Exposed to air	Thiosulfate Titer: Under nitrogen
		Ml.	*Ml.*
1	0.0005	2.44	..
2	0.005	4.42[a]	..
3	0.02	4.42	..
4	0.04	4.43	4.40
5	0.05	4.44	..
6	0.10	4.44	4.42
7	1.0	4.49	4.41
8	2.0	4.53	4.42
9	4.0	..	4.43

[a] Very slow end point.

Estimation of Iodine

Because the use of chlorine water in Winkler's method has several disadvantages, chief among which is the fact that high results (*8, 12, 13, 21, 23*) may be obtained, the employment of bromine as originally proposed by Bugarszky and Horwath (*3*) has been instituted for purposes of oxidation.

An accurately measured portion of the potassium iodide solution was transferred to a 125-ml. Erlenmeyer flask. After the addition of 1 ml. of 2 *N* sulfuric acid and sufficient water to give a total volume of 50 ml., bromine vapor was added as previously described. A few glass beads were introduced and the contents of the flask boiled briskly over a thin sand bath. After the yellow color due to bromine had disappeared, the boiling was continued for 2 minutes in order to insure complete removal of that element. Upon cooling to room temperature, the sides of the flask were washed down with sufficient water to replace that lost by boiling. One milliliter of a freshly prepared 10 per cent potassium iodide solution was added, the flask was gently swirled, and the liberated iodine immediately titrated with thiosulfate.

Table II gives the result of a typical experiment and shows that the Winkler procedure gives satisfactory results when the precautions given here are followed.

Table II. Determination of Iodine

Experiment	Total Volume	2*N* H_2SO_4	KI Added	0.00512 *N* $Na_2S_2O_3$	0.001024 *N* $Na_2S_2O_3$	Iodine Taken	Iodine Found	Difference
	Ml.	*Ml.*	*Gram*	*Ml.*	*Ml.*	*Mg.*	*Mg.*	*Mg.*
1	50	1	0.1	9.25	...	1.000	1.002	+0.002
2	25	0.5	0.05	4.64	...	0.501	0.502	+0.001
3	25	0.5	0.05	1.845	...	0.1995	0.200	+0.0005
4	10	0.2	0.02	...	4.54	0.1000	0.0983	−0.0017
5	10	0.2	0.02	...	2.27	0.0500	0.0492	−0.0008
6	10	0.2	0.02	...	0.915	0.0200	0.0198	−0.0002

Use of Salicylic Acid. It is the practice of some workers to add salicylic acid or phenol directly after boiling the solution in order to destroy any traces of residual bromine. This procedure was apparently substantiated by the observation that determinations of iodine in which salicylic acid was added were invariably lower than in those to which the compound was not added. Later, however, this interpretation was shown to be incorrect by subjecting iodate solutions to the same treatment. A lowering of titer manifested itself in those cases where salicylic acid had been introduced even though no bromine was present in the solution prior to this mode of treatment. Moreover, titrations of iodate solutions in which bromine had been added (no salicylic acid added) and then boiled off did not differ from those in which none of this element had been present. Salicylic acid, therefore, apparently offers a reducing action and must not be added.

The small amount of salicylic acid present as a preservative in the starch solution has no harmful effects.

Interference by Other Substances

Experiments on interference with the proposed procedure by certain elements and compounds were carried out according to the technic given above. In brief, the substance to be tested for its effect on the determination was added to 50 ml. of a solution containing 1 mg. of iodine and 1 ml. of 2 *N* sulfuric acid. The estimation of iodine was carried out in the usual manner.

Iron. When 0.1 mg. of iron was present, the results obtained were about 1 per cent too high, indicating that the added potassium iodide was being oxidized by the ferric salt. Correct figures were had when less than 0.1 mg. of iron was present. If the determination of iodine is carried out in the presence of larger amounts of iron, phosphoric acid should be added to remove the ferric ion.

Bromides. Since the oxidation of iodides by bromine is a reversible reaction, bromides may be expected to have some effect. It was found that no more than a twenty-fold excess of bromine over iodine could be present. When 30 mg. of bromine (as Br^-) were introduced, a 1 per cent loss of iodine took place and as much as a 30 per cent loss was observed when 50 mg. were present. Reith (*21*), on the other hand, has reported that a four hundred fold excess of the bromide ion may be present with no deleterious effects. This disagreement is probably due to the fact that he worked with quantities of 1 to 10 γ of iodine.

Nitrites. There should be little or no nitrites present. As small a quantity as 1 mg. of nitrous acid caused a 2 per cent loss of iodine. The azide method of Reith (*21*) was found to be highly effective in destroying even as much as 100 mg. of nitrous acid present in a determination.

Chlorides. Only large quantities of chlorides interfere.

Other Substances. Sulfates interfere only when present in a nearly saturated solution. Ammonium salts and nitrates apparently have no effect if present in moderate amounts. Mercury does not interfere until sufficient quantities (30 to 50 mg.) are contained in solution and precipitate as mercuric iodide when potassium iodide is added, thus obscuring the end point. Only traces of alcohol may be present; in the extraction of iodides with this substance care must be taken, therefore, that all alcohol is evaporated off.

Analysis of Iodized Salt

The use of iodized salt for the prevention of endemic goiter (*14*, *16*) is well known and various methods, both volumetric (*4*, *5*, *18*) and colorimetric (*6*, *24*), have been devised for the estimation of iodides in this product. The volumetric methods of Dunn and von Fellenberg were tested, but the results obtained were not satisfactory with iodine and sodium chloride mixtures comparable to the iodized salts as sold in America. Indeed, using the procedure of Dunn, losses of iodine as high as 50 per cent were experienced.

Table III. Determination of Iodine in Presence of Sodium Chloride

Experiment	NaCl Present[a]	0.00500 *N* $Na_2S_2O_3$	Iodine Added	Iodine Found	Difference
	Gram	*Ml.*	*Mg.*	*Mg.*	*Mg.*
1	20	5.37	1.000	0.568	−0.414
2	20	8.04	1.000	0.850	−0.150
3	10	9.40	1.000	0.994	−0.006
4	10	9.32	1.000	0.986	−0.014
5	5	9.45	1.000	0.999	−0.001
6	5	4.74	0.501	0.501	0.000
7	5	1.89	0.199	0.200	+0.001
8	5	0.95	0.100	0.101	+0.001

[a] Volume, 100 ml.

Effect of Chlorides. The estimation of iodides in iodized salt resolves itself to a matter of determination of iodine in the presence of large amounts of chlorides. Accordingly, experiments were carried out to ascertain the interference, if any, of salt on the determination. Sodium chloride (c. p.) was carefully recrystallized from alcohol and weighed portions were added to solutions containing a known amount of iodine and 2 ml. of 2 *N* sulfuric acid in a volume of 100 ml. The iodine was then determined by the procedure given above.

Results obtained (Table III) show that no more than 5 grams of sodium chloride should be present in 100 ml. of solution if accurate results are desired. It is to be noted that the methods of Dunn and von Fellenberg depend upon determination of the iodine in a 20 per cent solution of iodized salt. Doubtless this high salt concentration accounts for failure to obtain correct figures with their analytical procedure.

Analysis of Iodized Salt. The method finally adopted for the determination of iodine in iodized salt is as follows:

A 5-gram portion of the salt and 100 ml. of water were transferred to a 200-ml. Erlenmeyer flask and the contents of the vessel mixed until solution of the sodium chloride had taken place. Methyl orange indicator was added and 2 *N* sulfuric acid was introduced drop by drop until a pink color resulted which persisted on standing. (This treatment is necessary since table salts usually contain calcium phosphate or certain carbonates which are insoluble in neutral solution.) After the addition of 2 ml. of 2 *N* sulfuric acid and bromine vapor, a few glass beads were added and the solution boiled until the yellow color due to bromine had disappeared and then for 2 minutes longer. Upon cooling, the sides of the flask were washed down with approximately the amount of water lost by boiling, 2 ml. of a 10 per cent potassium iodide solution (freshly prepared) were added, the contents of the flask were gently swirled, and the liberated iodine was immediately titrated with 0.005 *N* thiosulfate, adding 2 ml. of starch indicator near the end point.

Analyses were made on several representative brands of iodized table salt as purchased on the open market. The results obtained are summarized in Table IV, and it can be seen that salts A, B_1, and B_2 contain an amount of potassium iodide which is far below their stated value. This is probably due to loss, since it has been shown by several investigators (*5*, *10*, *18*) that iodized salts may lose their iodine content with greater or less rapidity according to the form of the iodine compound contained, the presence of certain other elements in the salt, and the mode of storage.

Table IV. Determination of Potassium Iodide in Iodized Salt

Experiment	Brand	Weight of Sample	0.00500 *N* $Na_2S_2O_3$	KI Found	KI Claimed[a]
		Grams	*Ml.*	%	%
1	A	5.18	0.63	0.00168	0.01
2	A	5.40	0.64	0.00164	0.01
3	B_1	5.29	5.08	0.0133	0.023
4	B_1	5.42	5.10	0.0130	0.023
5	B_2	5.14	4.96	0.0133	0.023
6	B_2	5.05	4.91	0.0134	0.023
7	B_3	5.00	7.64	0.0211	0.023
8	B_3	5.00	7.64	0.0211	0.023
9	C	5.13	7.37	0.0199	0.02
10	C	5.12	7.42	0.0200	0.02

[a] Label statement.

As a final verification of the procedure, determinations of iodine recovery were carried out. Twenty-five grams of iodized salt (sample B_3) were dissolved in water and the volume was made up to 500 ml. after total solution by careful acidification as given above. Aliquot portions of 100 ml. were taken for analysis and are represented by experiments 7 and 8 in Table IV. To each of two other aliquot portions was added 0.501 mg. of iodine. After estimations of the total iodine present, it was found that 0.503 and 0.502 mg., respectively, of iodine were recovered.

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Errors in Determination of Carbonate in Boiler Waters

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From the results of adsorption tests on the Winkler method it is apparent that the method is susceptible to serious errors in the presence of sulfate. It will not prove satisfactory for boiler waters where the sulfate ion is present in appreciable concentrations.

The phenolphthalein–methyl orange titration is not accurate in solutions whose concentrations of carbonate are below 60 parts per million. At 30 parts per million of carbonate, the minimum possible error which may be expected is 26 per cent.

Methods have been suggested for improving the accuracy of this determination of carbonate. It is advised, however, that any method used for the determination of carbonate be checked by the evolution method (13) which is known to be accurate in practically all cases.

The concentration of carbonate present in a boiler water is ordinarily determined, in plant practice, by either the modified Winkler method (*9*) or the phenolphthalein–methylorange method (*1*). Like most analytical procedures for boiler waters, these two methods have been taken from the field of analysis of natural waters, and without material modification or very extensive checking have been applied directly to boiler waters. Between natural waters and boiler waters there are very material differences; and these differences are especially great in the case of the carbonate. In natural waters an extremely low concentration of hydroxide and a comparatively high concentration of carbonate are ordinarily found. In samples removed from a boiler the reverse is usually true.

The carbonate concentrations in a boiler treated with sodium carbonate for the prevention of scale usually run from 5 or 6 to 50 or 60 parts per million. In most natural waters the concentration of carbonate is above 60 parts per million. The extension of an analytical method to lower concentrations than those for which it has been designated will often cause the method to be inaccurate or perhaps fail altogether. As a considerable amount of previous work has shown (*13, 17*), and as will be shown in the present paper, the Winkler method and the phenolphthalein–methyl orange method for the determination of carbonate become inaccurate at low concentrations, but for different reasons. The Winkler method has been found to be inaccurate in the presence of sulfate; the phenolphthalein–methyl orange method because it has been extended to carbonate concentrations which are too low.

Winkler Method

The Winkler method, as applied to the determination of the carbonate concentration of a sample containing hydroxide and carbonate, consists in the titration of one sample directly to the phenolphthalein end point; a second sample, after the precipitation of the carbonate by the addition of barium chloride, is also titrated to the phenolphthalein end point. The difference in the amount of acid used in these two titrations is equivalent to the carbonate present.

The presence of sulfate in the samples causes the precipitation of the barium sulfate before barium carbonate is precipitated, because the sulfate is considerably more insoluble than the carbonate. The fact that the sulfate causes errors in the Winkler method has been definitely shown (*10, 13*). It seems desirable to ascertain whether the errors in the presence of sulfate are due to the occlusion or adsorption of hydroxide by the precipitate of barium sulfate. This would seem to be highly probable, since both barium sulfate and carbonate have been shown to occlude or adsorb many compounds (*2, 4, 5, 7, 8, 12, 14*).

Experimental Method. The method used consisted essentially in making up solutions of accurately known concentrations of hydroxide which contained sulfate, precipitating the sulfate as barium sulfate, and then titrating back the hydroxide to find how much was still present in the solution. This back-titration was performed both on the solution containing the precipitate and on an aliquot portion after the precipitate had been filtered off.

All the solutions used were made up with boiled distilled water and great care was exercised to keep them carbonate-free throughout the duration of the test. The carbonate-free sodium hydroxide was made up with sodium metal in the manner described by Clark (*3*). The sodium hydroxide solution was standardized against potassium acid phthalate. The hydrochloric acid solution was standardized against the hydroxide solution. An evolution analysis for carbonate was run on all the solutions and the distilled water used. This indicated that the maximum amount of carbonate which could be present in any of the samples titrated was less than 0.8 part per million. The sodium sulfate and the barium chloride solutions used were neutralized until the maximum possible error they could cause was less than 0.01 cc. of the titrating acid.

For those samples in which an aliquot was titrated the apparatus shown in Figure 1 was used. It consists essentially of a tower filled with soda lime and ascarite for removing carbon dioxide from the air which was to come in contact

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with the sample; the sample with the precipitate was held in the 100-cc. volumetric flask shown; this sample filtered down through the crucible into the lower suction flask. The crucible used had a porous bottom and over this were placed four layers of fine filter paper. After 10 minutes for precipitation at room temperature, a 100-cc. sample could be readily filtered in this equipment in 10 or 20 minutes, without having a chance to come in contact with the carbon dioxide of the air.

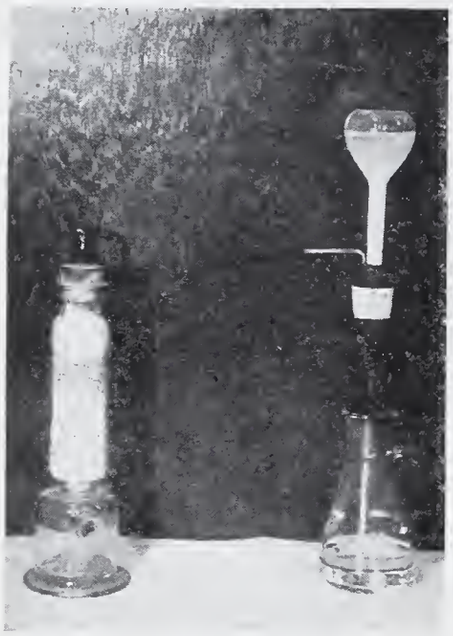

Figure 1. Apparatus for Filtering Off Barium Sulfate Precipitate

In the actual filtration of the sample the first 10 or 20 cc. were discarded to allow the filter paper to come to equilibrium with the solution, or the filter paper itself might have adsorbed hydroxide. The aliquot was then taken from the remainder. No correction was made for the change in the volume of the solution during precipitation. Some tests indicated that this change was about 0.25 cc., which would produce a difference of about 0.03 cc. on the titrating acid used. This was about within the limits of accuracy of the experiments on these titrations of the aliquots.

All pipets and burets used were calibrated and the measurement of the volume of the titrating acid used was made accurate within 0.02 cc.

Results of Titrations. Table I shows the results secured for a series of samples which were titrated back with acid in the presence of the barium sulfate precipitate. This represents, of course, the procedure generally used in the Winkler method where the precipitate is not filtered off.

Table I. Titration of Hydroxide in Presence of Barium Sulfate Precipitate

Sample	OH	SO_4	NaOH	HCl Required	HCl Used	CO_3 Equivalent
	P. p. m.	*P. p. m.*	*Cc.*	*Cc.*	*Cc.*	*P. p. m.*
5	102	300	10.00	12.35	12.10	7.3
	102	300	10.00	12.35	12.13	6.4
3	102	500	10.00	12.35[a]	12.13	6.4
	102	500	10.00	12.35	12.10	7.3
4	102	1500	10.00	12.35	11.87	13.9
	102	1500	10.00	12.35	11.86	14.2
6	254	500	25.00	30.94[a]	30.43	14.8
	254	500	25.00	30.94	30.43	14.8
7	254	1500	25.00	30.94	30.05	25.8
	254	1500	25.00	30.94	30.08	25.0

[a] Values determined by titration of a 100-cc. sample.

5 minutes for precipitation at room temperature. Stoppered.
10 cc. neutralized 10 per cent $BaCl_2$ added.
NaOH solution 0.05986 *N*.
HCl solution 0.04837 *N*.
100-cc. samples.

Since the hydrochloric acid required is the amount of acid necessary to titrate the sodium hydroxide added to the sample, the difference between this value and the hydrochloric acid used represents the amount of hydroxide which was occluded or adsorbed during the precipitation of the barium sulfate. This difference in the amount of acid used has been converted into carbonate equivalent in parts per million, exactly as if this analysis were being applied to the determination of carbonate. This carbonate equivalent really represents the positive error in the carbonate concentrations when the Winkler method is being applied to solutions of these concentrations of hydroxide and sulfate. As is seen, this error runs from about 7 to 25 parts per million of carbonate and, since in boiler waters we are usually dealing with concentrations from about 5 to 60 parts per million, this may cause an extremely large error. The error also tends to increase with increase in either the hydroxide or sulfate concentration.

Table II shows the results secured in titrating a 50-cc. aliquot after filtering off the precipitate of barium sulfate.

Table II. Titration of 50-cc. Aliquot after Filtering off Barium Sulfate

Sample	OH	SO_4	NaOH	HCl Required	HCl Used	CO_3 Equivalent[a]
	P. p. m.	*P. p. m.*	*Cc.*	*Cc.*	*Cc.*	*P. p. m.*
8	102	500	10.00	6.18[b]	5.74	25.6
	102	500	10.00	6.18	5.75	25.0
9	102	1500	10.00	6.18	5.57	35.4
	102	1500	10.00	6.18	5.66[c]	30.2
10	254	500	25.00	15.47[b]	14.83	37.2
11	254	1500	25.00	15.47	14.62	49.4

[a] Calculated on the basis of 100-cc. sample.
[b] Values determined by titration.
[c] Faint turbidity present in filtrate.

10 minutes for precipitation at room temperature.
10 cc. neutralized 10 per cent $BaCl_2$ added.
NaOH solution 0.05986 *N*.
HCl solution 0.04837 *N*.
100-cc. samples.

The fifth and sixth columns apply to the 50-cc. aliquot; twice the difference between the two would represent the amount of hydroxide adsorbed or occluded in the 100-cc. sample, the value used in the carbonate equivalent. This makes the last column in Tables I and II directly comparable and, as shown, the error is much larger in the filtered sample. This indicates that when the Winkler method is applied to solutions containing sulfate a larger error for adsorption or occlusion will occur when the precipitate is filtered off than when it is not. It is very possible that some of the adsorption of the hydroxide occurs on the surface of the barium sulfate precipitate and that, when the precipitate is left in the solution which is being titrated, a portion of the hydroxide on the surface may enter into the back-titration.

The adsorption or occlusion of hydroxide by the barium sulfate precipitate will, of course, cause some error in the determination of the hydroxide concentration as well as the carbonate. Since the hydroxide in boiler waters is usually high, and since an error of 10 parts per million in the carbonate corresponds to an error of only 3.5 parts per million of hydroxide, this will not be important in routine work. Where a high degree of accuracy is required for the hydroxide determination it may become important.

Straub has indicated (*16*) that the precipitation of sulfate in an alkaline solution does not produce serious errors in the determination of sulfate. This checks well with the present work which indicates that to some extent the hydroxide is adsorbed on the surface and this might be removed by exposure of the material to wash water, especially that containing carbon dioxide. The precipitates from the six filtered samples in Table II were washed with carbon dioxide–free water until the wash water was acid to phenolphthalein and were then placed in a solution of excess standard acid and allowed to stand, with occasional shaking, for 24 hours. On back-titration it was found that practically none of the excess acid was neutralized by the precipitate. This would indicate that the wash water may have, to a considerable extent, removed the hydroxide adsorbed on the surface and that the rest of the hydroxide was occluded in such a manner that it could not react with the acid.

Since the work which has been done shows that the Winkler method for carbonate is susceptible to large errors in the presence of sulfate, it would seem desirable to consider ways of removing this error. The use of strontium chloride instead of barium chloride for the precipitation of the carbonate has been found satisfactory; when strontium is used it is not necessary to precipitate the sulfate at all, and the strontium

carbonate precipitated does not occlude or adsorb enough hydroxide to produce a measurable error (*15*). The chief disadvantage with the use of strontium is that the sample in which the precipitation is carried out has to be boiled. At the present time this seems, however, to be the most satisfactory method for carbonate unless it is possible to use the evolution method (*13*).

Phenolphthalein–Methyl Orange Method

The application of the phenolphthalein–methyl orange method to a solution containing hydroxide and carbonate assumes that at the phenolphthalein end point all the hydroxide has been titrated and the carbonate has been titrated to bicarbonate; at the methyl orange end point the bicarbonate is assumed to have been converted to carbonic acid. From this reasoning the amount of acid used between the phenolphthalein and methyl orange end points is equivalent to the carbonate present in the sample. Several investigators have found that this method is not reliable at low concentrations of carbonate (*13*, *17*) and it has been found especially inaccurate in actual boiler-water samples. It seems desirable to ascertain if there is anything fundamentally wrong with this method at low concentrations of carbonate, and to determine at which concentrations it may be expected to become reasonably accurate. In order to do this, a series of titration curves for mixtures of hydroxide and carbonate were calculated.

Derivation of Equations. The equation for the titration curve—that is, the curve of pH against cubic centimeters of acid required to reach a given pH—is derived very simply by writing all the fundamental equations for the sample involved. Assuming a solution containing hydroxide, carbonate, sodium, and the indicators phenolphthalein and methyl orange which is being titrated with hydrochloric acid, the following equations may be written:

$$H_2CO_3 + HCO_3^- + CO_3^{--} = c_2 \quad (1)$$

$$Na^+ + H^+ = OH^- + HCO_3^- + 2(CO_3^{--}) + Cl^- + (In^-)_p + (In^-)_m \quad (2)$$

$$(H^+)\,(OH^-) = K_w = 10^{-14} \quad (3)$$

$$Na^+ = c_1 + 2c_2 \quad (4)$$

$$K' = \frac{(H^+)\,(HCO_3^-)}{H_2CO_3} = 3 \times 10^{-7} \quad (5)$$

$$K'' = \frac{(H^+)\,(CO_3^{--})}{HCO_3^-} = 6 \times 10^{-11} \quad (6)$$

$$K_p = \frac{(H^+)\,(In^-)_p}{(HIn)_p} = 1 \times 10^{-10} \quad (7)$$

$$K_m = \frac{(H^+)\,(In^-)_m}{(HIn)_m} = 5 \times 10^{-4} \quad (8)$$

Where c_1 = moles per liter of NaOH added
c_2 = moles per liter of Na_2CO_3 added
c_3 and c_4 = moles per liter of phenolphthalein and methyl orange added, respectively
HCO_3^- = moles per liter of HCO_3 ion in the solution, etc.
In = indicator

Equation 1 states that the sum of all the carbonate in the solution is equal to the total carbonate; 2 is the equation for the electroneutrality of the solution; 4 defines the total sodium present; 3, 5, and 6 are the equations for the dissociation of water, the first dissociation constant of carbonic acid, and the second dissociation constant of carbonic acid, respectively; and 7 and 8 are the dissociation constants of phenolphthalein and methyl orange, respectively.

Substituting in 2 so as to eliminate all the variables except Cl^-, which represents the mole per liter of acid added, and H^+ Equation 9 is obtained. The values for the various dissociation constants have also been inserted.

$$Cl^- = c_1 + 2c_2 + H^+ - \frac{K_w}{H^+} - 3c_2 \times 10^{-7}\left[\frac{H^+ + 1.2 \times 10^{-10}}{(H^+)^2 + 3 \times 10^{-7}(H^+) + 1.8 \times 10^{-17}}\right] - \frac{6 \times 10^{-15}}{H^+ + 10^{-10}} - \frac{5 \times 10^{-10}}{H^+ + 5 \times 10^{-4}} \quad (9)$$

This equation assumes that all the hydroxide has been added as sodium hydroxide and all the carbonate as sodium carbonate. The hydrolysis of the sodium carbonate is negligible because of the high initial pH of the samples dealt with. The concentration of phenolphthalein was assumed to be about that obtained when 4 drops of a 1 per cent solution are added to a 100-cc. sample ($c_3 = 6 \times 10^{-5}$); and of methyl orange that obtained when 4 drops of a 0.02 per cent solution are added to the same sample ($c_4 = 1 \times 10^{-6}$). The activity coefficients are used as unity and the effect of dilution due to the addition of the titrating acid is neglected. The effect of dilution, as will be shown later, is very small in such samples as are usually dealt with.

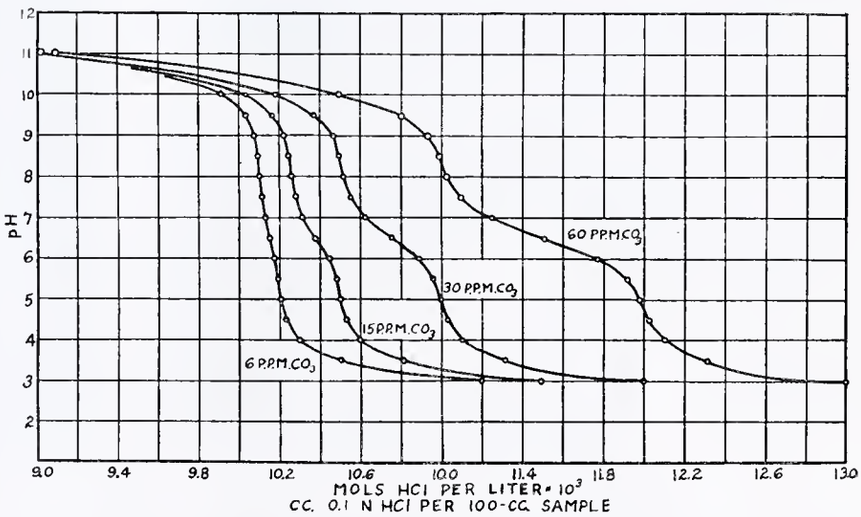

Figure 2. Titration Curves for Solutions Containing 170 P. p. m. Hydroxide and Various Concentrations of Carbonate

By selecting values for H^+ corresponding to every 0.5 pH and substituting them in Equation 9, the corresponding amount of acid (Cl^-) required to reach this pH is obtained. Using $c_1 = 10^{-2}$ (170 p. p. m. of OH) and $c_2 = 1 \times 10^{-4}$; 2.5×10^{-4}; 5.0×10^{-4}; and 1×10^{-3}; (6, 15, 30, and 60 p. p. m. of CO_3, respectively) a series of curves was calculated in the manner described.

Titration Curves. The curves secured are shown in Figure 2. In the case of the phenolphthalein end point it is evident that the reversal of the direction of the curve (inflection point) for the four curves shown always comes between a pH of 8 and 8.5. This inflection point comes sufficiently close to the colorless point of phenolphthalein (pH of about 8) so that the end point should be satisfactory. At higher concentrations of carbonate the slope of the curve in the region of the inflection point is less, and this causes a slow color change which will make an accurate determination of the end point somewhat difficult. For the concentrations shown on this figure the phenolphthalein end point should be fairly satisfactory.

In the case of the methyl orange end point a number of difficulties appear. The methyl orange end point may be taken as a pH of 3.9 corresponding to 20 per cent converted to

the acid form. This is about the pH that would ordinarily be attained in routine practice when a color comparison solution is not used. It is seen from Figure 2 that the lower inflection points occur at a much higher pH than this value of 3.9 for the methyl orange end point. At a pH of 3.9 the curves are very flat. This will make the color change extremely slow and the end point difficult to detect. It is apparent in this region that a considerable amount of acid may be added with only a small change in the pH.

A more startling fact appears, however, if the amount of acid which should be required to titrate the carbonate in the 6 parts per million sample, on the basis of the regular phenolphthalein–methyl orange calculations, is compared to the amount actually used for this titration as shown by the

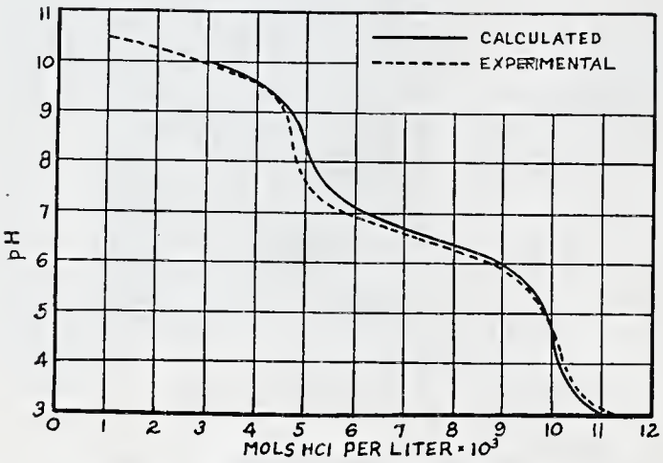

Figure 3. Comparison of Calculated with Experimental Curve

curve. Six parts per million of carbonate are 0.1 millimole per liter. By the usual phenolphthalein–methyl orange calculations this would require 0.10 millimole of hydrochloric acid per liter for titration or on this plot would require from 10.10 to 10.20 millimoles of hydrochloric acid. Actually, to go from pH 8.3 to 3.9 requires from 10.1 to 10.32 millimoles of acid; 0.22 millimole has been used instead of the required 0.10 millimole. This is an error of 120 per cent. The rest of the curves show similar errors, the percentage error decreasing, however, as the carbonate increases. To a large extent this error is due to the presence of the water in the sample which is not taken account of in the assumptions on which the phenolphthalein–methyl orange method is based.

Table III shows the millimoles per liter of acid which would be required to titrate the carbonate present in these four samples between the phenolphthalein and methyl orange end points according to the usual calculations, the millimoles per liter of acid used according to the curves, and the per cent error in the carbonate. The conclusion that the phenolphthalein–methyl orange method is too inaccurate to be used for even routine work on samples containing less than 60 parts per million of carbonate is inescapable.

Table III. Error in Determination of Carbonate Using Phenolphthalein–Methyl Orange Titration

CO_3	HCl Required[a]	HCl Used[b]	CO_3 Error
P. p. m.	*Millimoles/l.*	*Millimoles/l.*	%
6	0.10	0.22	120
15	0.25	0.37	48
30	0.50	0.63	26
60	1.00	1.14	14

[a] Based on usual phenolphthalein–methyl orange calculations.
[b] Determined from acid required to titrate between pH 8.3 and 3.9 according to curves in Figure 2.

Moreover, the errors shown represent the absolute minimum error that may be expected. The effect of dilution and loss of carbon dioxide during the titration, the possibility of the samples picking up carbon dioxide when it is alkaline, and the effect of organic matter or buffer salts in the solution will all tend to increase the size of this error.

In order to demonstrate the accuracy of the method of calculation used, a calculated curve was compared with an experimental curve as shown in Figure 3. These curves are for 300 parts per million of carbonate. The experimental curve was taken from the curves published by Greenfield and Buswell (*6*), and is for 0.01*M* solution, using a rocking hydrogen electrode. The values secured using the bubbling hydrogen electrode (*11*) cannot be compared with the calculated curve, because the flow of hydrogen removes too much carbon dioxide from the sample.

Figure 3 shows extremely good agreement, the maximum deviation being only 0.3 millimole. The inflection points on both curves occur at the same pH. As predicted, the experimental curve actually shows a larger error than the calculated curve. The effect of dilution by the titrating acid was determined for this calculated curve and is less than 0.02 millimole except at a pH of 3.0 where it becomes 0.10 millimole. The effect tends to bring the experimental and calculated curves into slightly better agreement.

The curve in Figure 2 shows that the lower inflection point drops from a pH of about 5.3 to about 4.60 as the carbonate increases from 6 to 60 parts per million. The upper inflection point remains almost constant at about 8.3. Substituting $H^+ = e^{-2.303n}$ in Equation 9, differentiating twice, and setting the second derivative equal to zero an equation in H^+ alone may be secured from which the actual inflection points may be accurately calculated.

The equation finally secured is the following:

$$0 = 1 - \frac{K_w}{(H^+)^2} - c_2 \times \left[\frac{(H^+)^4 - 3 \times 10^{-7}(H^+)^3 + 5.4 \times 10^{-24}(H^+) - 3.24 \times 10^{-34}}{[(H^+)^2 + 3 \times 10^{-7}(H^+) + 1.8 \times 10^{-17}]^3}\right] \quad (10)$$

Using different values of c_2 (the carbonate concentration) this equation may be solved for H^+. The upper inflection point—that is, the phenolphthalein end point—will be found to be independent of concentration of carbonate and always occurs between a pH of 8.36 and 8.37.

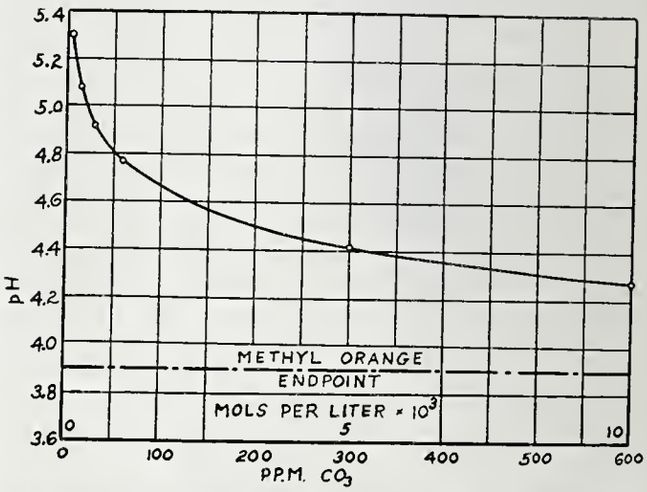

Figure 4. Change of Methyl Orange Inflection Point with Concentration of Carbonate

The position of the lower inflection point, which is supposed to be measured by the methyl orange end point, as was indicated by Figure 2, is dependent on the concentration of carbonate present. Figure 4 shows how the position of the inflection point varies with carbonate concentration. The position of the methyl orange end point (pH of 3.9) is marked on this chart and deviates most widely from the inflection

point at low carbonate concentrations. This shows, again, why the phenolphthalein–methyl orange titration is so inaccurate at low concentrations. The curve shown crosses the pH of 3.9 around 6000 parts per million of carbonate (0.10 *M*) and at this point the titration should be quite accurate. This is found to be true experimentally.

Calculations were made to see if the position of the inflection points agreed with the stoichiometric values for the titration of bicarbonate to carbonic acid as assumed in the phenolphthalein–methyl orange method. At the upper pH the position of the inflection point was always within 0.02 per cent of the correct position. At the lower pH the maximum deviation was 0.4 per cent. These errors are not serious and it is not the deviation of the inflection point from the stoichiometric equivalent point that causes the errors, but the fact that the pH of the lower inflection point changes with concentration and that in low concentrations of carbonate the indicator is not properly selected to give the correct end point.

The accuracy of the method might be improved by using an indicator which changes color at a higher pH than methyl orange. If such an attempt is made, it is absolutely necessary that accurate color comparison blanks should be prepared which will indicate the correct end points. One difficulty with such a method is the necessity of knowing the approximate carbonate concentration in order to select the correct end point. Another possible source of error that will have to be guarded against is salt errors in the indicators. If an attempt is made to use different indicators on boiler waters, it seems absolutely necessary that the method should be checked at least occasionally (*13*).

Acknowledgment

The author is very much indebted to L. O. Case of the University of Michigan for many helpful suggestions concerning this paper.

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Composition of Fatty Acid Mixtures

I. Relation of Composition to Dalican's Curve

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In the manufacture of commercial fatty acids, it is customary to estimate cold press yields from the titers of pressroom products by making use of a table of empirical data showing the percentages of commercial oleic acid and commercial stearic acid in mixtures of different titer. Such data are extremely useful in the control of plant operations, but their purely empirical nature and correspondingly limited applicability must always be kept in mind. Thus, while it is perhaps generally recognized as hazardous to apply the same set of data to stocks differing widely in source, it is not as generally realized that, even in the case of a single stock, such calculations give no reliable information whatever regarding the actual percentages of saturated and unsaturated fatty acids present.

There are two important considerations involved here, neither of which must be lost sight of. In the first place, when a solid fraction is separated from a fatty acid mixture by cooling, both fractions are solutions and each contains all components present in the original mixture. The solid which separates, considered apart from any entrained or adsorbed liquid, is a solid solution—that is, a wholly solid phase containing, however, components that are themselves (when alone, but not now) liquids, just as a solution of salts in water is wholly liquid although it contains components that are, when alone, solids. Similarly, the liquid fraction contains solid fatty acids in solution and, as will be seen, a considerable percentage of these dissolved solid acids can never be separated, even theoretically, by chilling.

A second and more important consideration is the fact that the customary analytical methods applied to the original mixture and to the end products are themselves impossible of interpretation, in any exact way, in terms of fatty acid composition. The free fatty acid value assumes an average molecular weight which is purely arbitrary or involves assumptions as to composition. The iodine value assumes the presence of only mono-unsaturated acids unless combined with the thiocyanogen iodine value which has brought a notable advance in analytical procedures by providing an index to more highly unsaturated acids. In either event, the analytical results are controlled by the purely empirical time factor involved in the iodine value. This reaction time was established originally by working with some known product and assuming that the proper time for the method is the time in which, in this case, the amount of substitution that one does get just makes up for enough of the addition at double bonds that one does not get, to give, as a result, exactly the iodine value that one started out to get. And, in the reaction mixture in which this time was thus determined, the highly sensitive and all-important reaction velocities were necessarily different than in the case of the mixtures later analyzed, because of considerable differences in chemical environment.

It is the writer's conviction that only by perfecting methods that determine individual fatty acid components directly can fatty acid and soap chemists hope to build up reliable conceptions of the composition and changes of composition of their stocks in process. Because of the closely similar chemi-

cal properties of the fatty acids, such methods are certain to be physical-chemical methods. One of these is the mixed-melting point method developed by Twitchell (*7*) and later used by McGregor and Beal (*6*) in their study of the composition of menhaden oil. Further improvements in this method have more recently been made and will be described in a later communication.

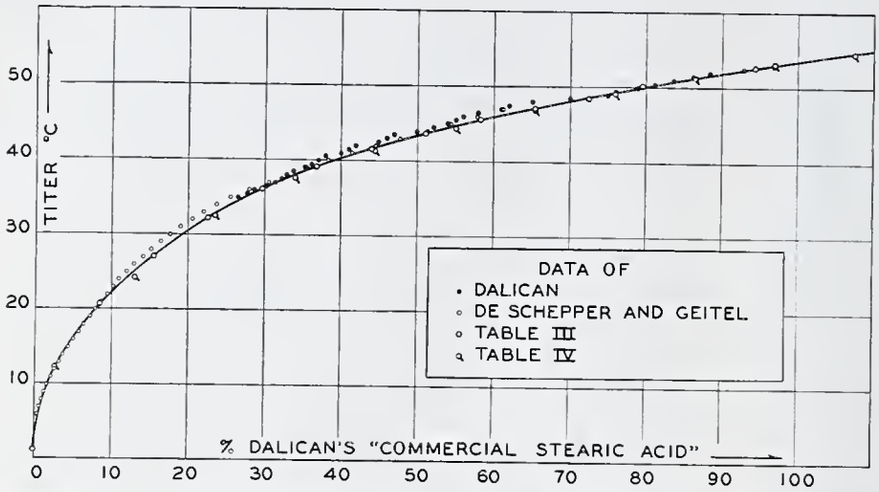

Figure 1. Dalican Curve Showing Titers of Fatty Acid Mixtures as a Function of Their Content of Commercial Stearic Acid

The present paper discusses the use of a table of data published originally in 1868 by Dalican, who devised the titer test itself, and still used to determine yields in the pressing operation. Dalican's data, modified to apply to the fatty acids rather than to their glycerides, and extended to lower titers by means of similar data published by de Schepper and Geitel (*2*), are presented graphically and compared with titers obtained from present-day commercial stocks. The important relation between the composition of fatty acid mixtures and their melting points, or titers, is also shown graphically for the simple palmitic-stearic-oleic system in a way which makes clear the effect of the presence of linolic acid in such a system and just how Dalican's curve fits into this picture.

Dalican's Table

In the separation of solid from liquid fatty acid by pressing, it is obvious that if the percentages of stearic acid in the stock charged, in the oil and in the press cake, can be estimated from their respective titers, then the yield follows at once from the fact that the amount of stearic acid in the two fractions must equal that in the original mixture before pressing.

Data for this purpose are furnished by Dalican's table as printed in Lewkowitsch (*4*). This table shows yields of commercial stearic acid and commercial oleic acid obtainable from fats of different titer. The figures are based on the glycerides and thus add in each case to 95 per cent. By dividing by 0.95, yields on the free fatty acid basis are obtained.

For lower titers, extension can be made on the basis of a similar table by de Schepper and Geitel (*2*), also reproduced in Lewkowitsch (*5*). This table is not directly comparable with Dalican's, since it gives percentages of "stearin" of solidifying point 48° C., whereas Dalican's stearic acid was evidently of about 54° C. titer. According to Dalican's data, a stock of 48° C. titer contains 65 per cent commercial stearic acid. The data of de Schepper and Geitel can, therefore, be expressed in terms of Dalican's stearic acid by multiplying by 0.65.

Dalican's data and those of de Schepper and Geitel, thus converted to the same basis, are given in Tables I and II.

It should, of course, be apparent from the fact that stocks of widely different chemical composition might have the same titer, that the data of Dalican and of de Schepper and Geitel cannot hold in any absolute way. For stocks that are fairly uniform as to source and are blended according to a fixed formula, however, an empirical relationship of that sort should hold with but little variation. De Schepper and Geitel stress this point particularly. They show the wide difference in the curves for palm oil, for tallow, and for mixtures of the two and they recommend that works chemists establish their own data with their own stocks.

The following experiments constitute such a check with commercial fatty acid stocks:

A sample of 1842 grams of run-off fatty acids, titer 38.95° C., was pressed at 24° C. for 10 minutes at 5000 pounds per square inch in a laboratory press; 569.5 grams (38 per cent) of pressed cake were obtained, having a titer of 50.15° C. The titer of the oil was 20.70° C. Samples of the oil and cake were then recombined in accurately weighed proportions and the titers of the mixtures recorded.

By pressing at 32.2° C., 357.2 grams of cake from the above experiment were further separated, giving a cake of 52.80° C. titer and an oil of 36.00° C. titer. The yield of cake here was 77.2 per cent.

Four hundred grams of the cold pressed oil were cooled in a refrigerator overnight and then placed in an ice bath while 30.5 grams of oil were drawn off from the semisolid mass through a cloth filter. The titer of this oil was 1.1° C., while that of the remaining 92.4 per cent was 21.45° C.

Table I. Dalican's Table

Titer	Commercial Stearic Acid		Titer	Commercial Stearic Acid	
	Fat basis	Fatty acid basis		Fat basis	Fatty acid basis
° C.	%	%	° C.	%	%
35	25.20	26.53	44.5	49.40	52.00
35.5	26.40	27.79	45	51.30	54.00
36	27.30	28.74	45.5	52.25	55.00
36.5	28.75	30.26	46	53.20	56.00
37	29.80	31.37	46.5	55.10	58.00
37.5	30.60	32.21	47	57.95	61.00
38	31.25	32.90	47.5	58.90	62.00
38.5	32.15	33.84	48	61.75	65.00
39	33.44	35.20	48.5	66.50	70.00
39.5	34.30	36.10	49	71.25	75.00
40	35.15	37.00	49.5	72.20	76.00
40.5	36.10	38.00	50	75.05	79.00
41	38.00	40.00	50.5	77.10	81.16
41.5	38.95	41.03	51	79.50	83.69
42	39.90	42.00	51.5	81.90	86.21
42.5	42.75	45.00	52	84.00	88.42
43	43.70	46.00	52.5	88.30	92.95
43.5	44.65	47.00	53	92.10	96.95
44	47.50	50.00			

Table II. Data of de Schepper and Geitel Converted to Basis of Dalican's Table

Solidifying Point	Stearin of Solidifying Pt. 48° C.	Dalican's Com'l Stearic Acid	Solidifying Point	Stearin of Solidifying Pt. 48° C.	Dalican's Com'l Stearic Acid
° C.	%	%	° C.	%	%
6	0.3	0.2	28	23.3	15.1
7	0.8	0.5	29	25.2	16.4
8	1.2	0.8	30	27.2	17.7
9	1.7	1.1	31	29.2	19.0
10	2.5	1.6	32	31.5	20.5
11	3.2	2.1	33	33.8	22.0
12	3.8	2.5	34	36.6	23.8
13	4.7	3.1	35	39.5	25.7
14	5.6	3.6	36	43.0	28.0
15	6.6	4.3	37	46.9	30.5
16	7.7	5.0	38	50.5	32.8
17	8.8	5.7	39	54.5	35.4
18	9.8	6.3	40	58.9	38.3
19	11.1	7.2	41	63.6	41.4
20	12.1	7.9	42	68.5	44.5
21	13.2	8.6	43	73.5	47.8
22	14.5	9.4	44	78.9	51.3
23	15.7	10.2	45	83.5	54.3
24	17.0	11.0	46	89.0	57.9
25	18.5	12.0	47	94.1	61.1
26	20.0	13.0	48	100.0	65.0
27	21.7	14.1			

According to the data of Tables I and II, the cold pressed cake, having a titer of 50.15° C., contained 79.6 per cent commercial stearic acid, and the cold pressed oil, titer 20.7° C., contained 8.4 per cent. If we accept these two values, the composition of the other samples, in terms of Dalican's "commercial stearic acid," is determined by the percentages of the intermediate mixtures and the yields obtained in the hot pressing and chilling experiments. The results are given in Table III.

Table III. Titers of Technical Fatty Acid Mixtures of Varying Commercial Stearic Acid Content

Sample	Cold Pressed Oil	Cold Pressed Cake	Titer	Dalican's Commercial Stearic Acid
	%	%	° C.	%
1	100.0	..	20.70	8.4
2	90.0	10.0	27.05	15.5
3	80.0	20.0	32.20	22.6
4	70.0	30.0	36.20	29.8
5	60.0	40.0	39.10	36.9
6	50.0	50.0	41.60	44.0
7	40.0	60.0	43.70	51.1
8	30.0	70.0	45.60	58.2
9	20.0	80.0	47.10	65.4
10	10.0	90.0	48.65	72.5
11	..	100.0	50.15	79.6
12	Hot pressed cake		52.80	94.4
13	Chilled oil		1.10	−0.1

A second series of values was obtained by determining the titers of mixtures made up from commercial grades of double-pressed distilled stearic acid and double-distilled red oil. These results are given in Table IV. Conversion to the basis of Dalican's commercial stearic acid was made by accepting the published data for mixtures having the titers of samples 1 and 10. Sample 11 is thus found to contain 107.5 per cent of Dalican's stearic acid, a figure which results from the fact that it has a higher titer than the sample Dalican used.

Table IV. Titers of Mixtures of Commercial Stearic Acid and Red Oil

Sample	Commercial Stearic Acid	Commercial Red Oil	Titer	Dalican's Commercial Stearic Acid
	%	%	° C.	%
1		100.00	12.25	2.5
2	10.00	90.00	24.25	13.0
3	20.00	80.00	32.53	23.5
4	30.00	70.00	37.72	34.0
5	39.97	60.03	41.19	44.5
6	50.00	50.00	44.29	55.0
7	60.00	40.00	46.92	65.5
8	70.00	30.00	49.26	76.0
9	79.96	20.04	51.29	86.5
10	89.96	10.04	53.11	97.0
11	100.00	...	54.70	107.5

In taking the titers the standard procedure was carefully followed. The thermometer used was standardized by comparison with a thermometer certified by the U. S. Bureau of Standards and corrections were made for the temperature of the emergent stem.

The results of these experiments, together with the data of Dalican and de Schepper and Geitel, are shown graphically in Figure 1.

Titers of Fatty Acid Mixtures

The relation of titer to composition in technical fatty acid mixtures is most readily visualized by considering the three-dimensional diagram, Figure 2.

Here the actual situation is simplified by considering all mixtures as composed of only palmitic, stearic, and oleic acids. The base, P' S' O', is the familiar triangular composition diagram within which any point represents a definite mixture of three components, in this case palmitic, stearic, and oleic acids. Titers are laid out on the vertical, temperature scale. The titers of all possible mixtures thus determine a surface, *OASJPBO*, with peaks at the three points *P*, *S*, and *O*, representing the individual acids and a minimum at some point, *C*. Contours of this surface, such as shown at *TUV*, if projected onto the base, give lines of constant titer on the composition diagram. Data giving the position of such lines have been published by Carlinfanti and Levi-Malvano (*1*). The intersections of the titer surface with the sides of the triangular prism are titer curves for the three binary mixtures and have the shapes indicated.

The lowest region of this titer surface is of particular interest. The position of the point *B* has been carefully investigated by Lapworth and Pearson (*3*), using highly purified palmitic and oleic acids, and found to be at 7.2 per cent palmitic acid. This means that crystallization and pressing of mixtures of oleic and palmitic acids containing more than 7.2 per cent palmitic acid to begin with, can never produce an oil carrying less than 7.2 per cent palmitic acid. The corresponding point, *A*, on the stearic-oleic curve has apparently never been investigated. It is apparent, however, that whatever the composition at *A*, the oil which is saturated with palmitic acid at *B* would take up still more solid acid at that temperature if the added acid were stearic. Addition of stearic acid to the mixture at *B* would change the composition along the line *BX*. The mixture would then be unsaturated and remain liquid until it again met the titer surface at *W*.

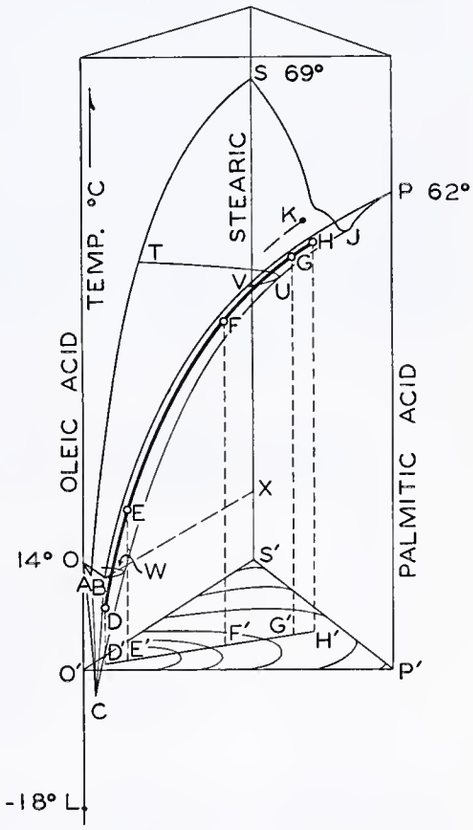

Figure 2. Titer Diagram for System Palmitic Acid–Stearic Acid–Oleic Acid

Addition of stearic acid to the mixture at *B*, or palmitic acid to that at *A*, would cause a further depression of the crystallizing point until finally a ternary eutectic would be encountered at *C*. The position of this point has never been established. It might require less than 7 per cent of solid acids or it might require considerably more.

It is interesting to note that Carlinfanti and Levi-Malvano did not encounter the eutectics *A* and *B* at all when they mixed their oleic acid with palmitic and with stearic. As pointed out by Lapworth and Pearson (*3*), this can only mean that their supposedly pure oleic acid contained more than 7 per cent of palmitic acid and an unknown amount of stearic acid dissolved in it. Their diagram of solidifying points for ternary mixtures is therefore also in error to that extent.

Dalican Curve on Titer Surface

Consider now the curve *DEFGH* which corresponds to the Dalican curve. The upper point *H* represents the composition and titer of the commercial stearic acid used, the point *D* that of the red oil. Neither is a fixed point. *H* will be closer to *SJP* the more completely the liquid acids are removed. It will shift back and forth with the ratio of palmitic to stearic

in the solid acids and this ratio may vary considerably in the different stocks. If it takes up a new position, as at K, this will involve a change in both position and shape of the entire curve.

So also with the lower point D. At this end of the curve, wide variation in position is possible because of variation in the amount of linoleic acid present with the oleic. For oleic acid the position of O would be at +14° C., for linoleic it would be at −18° C., and for intermediate proportions it might be anywhere between, or even considerably lower because a curve for these two acids would drop to a minimum of its own.

It is particularly to be noticed that with a drop in the position of O the titer surface will cut the horizontal plane representing any one temperature at positions farther from the liquid acid edge of the diagram. In other words, with increase in linoleic acid content, an oil of 10° C. titer will also carry higher percentages of the saturated acids. This higher saturated acid content, of course, exerts a partially compensating effect on the iodine value.

Oils of 0° C. titer, or lower, can readily be obtained from commercial mixtures. This is probably due more to the lowered position of point O, caused by linoleic acid, than to the steepness of the curve OC shown in the diagram.

One other point should be noted. Since Dalican's mixtures are all made up from the two stocks D and H, they all have compositions which can be represented on the triangular diagram by a straight line, $D'H'$. This is not necessarily true of the stocks actually handled in the plant to arrive at the products D and H, since these two cannot exist as liquid and solid phase in equilibrium with each other in any mixture and so can only be arrived at by a series of operations.

Enough has perhaps been said to show that the Dalican curve is at best only an approximation which must be handled with considerable caution even in its proper application, which is the estimation of probable yields of commercial products. It can contribute no evidence of an exact quantitative nature regarding the actual content of saturated fatty acids in any technical mixture.

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Titration of Ammonia in Presence of Boric Acid

Macro- and Micro-Kjeldahl Procedures

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The device of receiving in boric acid solution the ammonia distilled during the Kjeldahl analysis, suggested in 1913 by Winkler (*11*), has been reported upon favorably by several workers (*1*, *2*, *7*, *8*), and especially by Markley and Hann (*5*). That this procedure does not more rapidly displace the less convenient excess-acid method is perhaps due in part to difficulty with the end point, for the indicators recommended—e. g., bromophenol blue, methyl red, methyl orange, and congo red—are not very satisfactory when used in the ordinary manner in presence of boric acid, the color changes being too gradual or too slight to be perceived sharply except after practice or by use of special light. Bromophenol blue has been considerably used, as in the extensive trials of the boric acid absorption method by Scales and Harrison (*7*), Spears (*8*), and Markley and Hann (*5*), with empirical correction (included in the over-all blank) for the effects of boric acid and dilution upon the indicator, but apparently none for any effect due to ammonium salt, reported by Kolthoff (*4*) and by Stover and Sandin (*9*) to be marked.

Preliminary trials suggested the probable advantage in the use of an indicator which in presence of boric acid develops its acid color in an intermediate intensity which within a limited range is proportional to the acidity, and which is suitable for accurate color-matching. With such an indicator the end point of the titration can be detected by matching the color of a control liquid which contains the same quantity of boric acid and the same amount of indicator in the same volume. The titration will thus be completed in the acid region, but always at the pH of the diluted boric acid solution. The effect of the boric acid upon the indicator is the same in the color standard and the analysis, and therefore cancels out.

Methyl red fully meets the requirements mentioned, and in addition its salt error is negligible, as was shown by Thomson (*10*) and in the course of the present study. Its suitability for the color-matching titration was demonstrated some years ago, and the resulting procedure has been used successfully in numerous Kjeldahl analyses, many by inexperienced students. Recently Stover and Sandin (*9*) reported the use of a color-matching titration in the micro-Kjeldahl method with boric acid absorption, the preferred indicators being a mixture of tetrabromophenol blue and methyl red, and of methylene blue and methyl red. There is described below a titration procedure like that of Stover and Sandin, but extended to both macro- and microtitrations. Methyl red is used as indicator, and gives an end point which is definite and unmistakable without use of special light.

Macrotitration in Presence of Boric Acid

Erlenmeyer flasks of 500 cc. capacity are used. The color control is prepared by dilution (with carbon dioxide–free water) of 50 cc. of 4 per cent boric acid solution to a volume equal to or slightly greater than the final volume of the distillate liquid at the end of the titration of ammonia (about 250 cc.), and addition of 2 to 4 drops of 0.1 per cent solution of methyl red in 95 per cent alcohol. The control liquid should be clear pink or red; a moderately pronounced red color seems best, very pale or very deep colors being less easily matched. If the flask is tightly stoppered the color

standard can be used for a day or more. For absorption of ammonia 50 cc. of the same 4 per cent boric acid solution and as many drops of indicator as were added to the color control are taken. After distillation of the ammonia the cold liquid is titrated with 0.1 *N* acid, with the color control beside the distillate liquid, both flasks resting upon a white surface. The first faint orange or pink color which persists signals the approach of the end point. The titration is continued slowly until the colors of the two liquids are identical in intensity, the volumes being equalized (±10 cc.) if necessary by addition of water (best carbon dioxide–free if considerable is required). If the matching is properly done, 0.5 drop more of acid will markedly increase the intensity of the color as compared with that of the control. The color-matching can be accomplished with ease and precision, a variation of 0.01 to 0.02 cc. of 0.1 *N* acid being readily detectable. The addition (to the color control) of pure ammonium salt approximately equal to that formed in the titration is optional, but its effect is so small as to be negligible.

Microtitration in Presence of Boric Acid

The procedure is that given for the macrotitration, with suitable reduction in scale. There are used 100-cc. Erlenmeyer flasks with like dimensions and prepared as described by Pregl (*6*), 5 cc. of 4 per cent boric acid solution (measured with a pipet), and about 2 drops of 0.05 per cent methyl red indicator (enough to yield in the control liquid a distinct pink color), in a final volume of 35 to 40 cc. Water used in the color control and for volume adjustment should be free from carbon dioxide. The end point can be located within 0.01 cc. of 0.01 *N* acid.

Standardization of Acid for Titration

The 0.1 *N* and 0.01 *N* acids were standardized against sodium carbonate (De Haen's guaranteed, previously gently ignited), using methyl red indicator. Standardizations were made both by the color-matching titration in presence of boric acid, and by the usual procedure in its absence. In every case the liquid was boiled just before the true end point, then cooled rapidly and the titration completed. The color controls were likewise boiled. Normalities by the two methods were identical, showing that the titration of alkali in presence of boric acid by the color-matching procedure described is accurate, and that acid to be used in this procedure may be standardized in either way. Some results appear in Table I, which includes also values obtained by use of methyl red–methylene blue indicator, recommended by Johnson and Green (*3*) and tested by Stover and Sandin (*9*).

Table I. Standardization of 0.1 *N* and 0.01 *N* Hydrochloric Acid with Sodium Carbonate in Presence and Absence of Boric Acid

Indicator	Normality of Acid: In presence of boric acid, by color-matching titration	Normality of Acid: In absence of boric acid, by usual standardization procedure[a]
Macro:		
Methyl red	0.12615	0.12615
	0.12620	0.12620
	Av. 0.12618	Av. 0.12618
Micro:		
Methyl red	0.01189	0.01188 (first pink)
	0.01188	0.01188
	0.01188	Av. 0.01188
	Av. 0.01188	
Methyl red–methylene blue	0.01188	0.01188 (first violet)
	0.01189	0.01189
	0.01188	Av. 0.01189
	Av. 0.01188	

[a] Color blanks deducted.

Deterioration of Boric Acid Solution

Freshly prepared boric acid solution, diluted as specified above, gives with methyl red a pronounced acid color. Upon storage for some time the solution affects methyl red less strongly, and eventually fails to yield a red color. The explanation for this change is being sought; it may be the passage of alkaline constituents from the glass container into the boric acid solution, which may thus be partially buffered. While it is perhaps best to use an undeteriorated solution, it has been found that one which has deteriorated can be made usable by treating the whole stock solution with 0.1 *N* or 0.5 *N* acid until a portion properly diluted yields with methyl red an approximately normal red color. The color need not be exactly that imparted by a fresh boric acid solution; it need only be some tone of red which is suitable for color-matching. Since the restored solution will be used in equal amounts in both color standards and analyses, the total effect of the boric acid, etc., is automatically compensated.

Recovery of Ammonia

Aliquots of a standard solution of pure ammonium chloride were transferred to a micro-Kjeldahl apparatus and made alkaline; the ammonia was distilled into 5 cc. of 4 per cent boric acid solution and titrated with 0.01 *N* hydrochloric acid by the color-matching procedure. Methyl red and a mixture of methyl red and methylene blue were used as indicators, in two series of trials. Results are given in Table II.

Table II. Recovery of Ammonia Distilled from Ammonium Chloride by Micro-Kjeldahl Procedure, Using Color-Matching Titration

Indicator	Nitrogen Taken[a]	Nitrogen Found
	Mg.	*Mg.*
Methyl red	1.209	1.210
		1.208
		1.208
		1.207
		1.208
		1.207
		1.208
		1.208
		1.207
		Av. 1.208
Methyl red–methylene blue	1.209	1.208
		1.207
		1.207
		1.208
		1.208
		1.208
		Av. 1.208

[a] 10-cc. aliquots of solution of 0.4619 gram of ammonium chloride (De Haen's guaranteed) in 1000 cc.

The results in Table II represent a recovery of 99.9 per cent of the ammonia, using either indicator. Results with the two indicators are in better agreement than was found by Stover and Sandin. While both indicators are satisfactory, and even though the mixed indicator signals the approach of the end point earlier, it is thought that the color-matching at the end point is sharper and more certain with methyl red. The final colors of the mixed indicator are composites of the increasingly strong red of the methyl red and the color of the methylene blue, and these intermediate tones are less easy to match.

In Table III are collected results of some nitrogen analyses by both macro- and micromethods using the boric acid modification described. A number of results by the excess-acid procedure are included for comparison. Methyl red was used as indicator. In all cases over-all blanks were run, using sucrose, and suitable corrections applied.

As shown by the results in Tables II and III, ammonia distilled by the macro- or micro-Kjeldahl method and absorbed in boric acid solution can be titrated accurately with methyl red indicator, the end point being recognized by matching the color of a control liquid of the same volume and containing the same quantities of boric acid and of indicator. The titration can be made with normal rapidity.

The advantages of the proposed color-matching titration are the following: (1) the end point in presence of boric acid is sharp and unmistakable, and can readily be tested

Table III. Nitrogen Analyses by Boric Acid Modification of Kjeldahl Method, Using Color-Matching Titration with Methyl Red Indicator

Compound	Nitrogen Calc.	Nitrogen Found: Macromethod[a] Excess-acid procedure	Nitrogen Found: Macromethod[a] Boric acid absorption	Nitrogen Found: Micromethod[b] Boric acid absorption	Nitrogen Found: Micromethod[b] Excess-acid
	%	%	%	%	%
Urea	46.66	46.60	...	46.5	
		46.51		46.2	
		46.65		46.8	
		46.80		46.3	
		Av. 46.64		Av. 46.5	
p-Aminophenol–hydrochloride (Cl = 24.0%; calc. 24.4%)	9.62	9.45	9.48	9.37	9.47
		9.45	9.44	9.47	9.46
		Av. 9.45	9.49	9.48	9.45
			9.50	Av. 9.44	Av. 9.46
			9.46		
			Av. 9.47		
Glycine	18.67	18.73	18.51	18.6	
		18.79	18.78	18.6	
		18.78	18.69	Av. 18.6	
		Av. 18.77	18.73		
			Av. 18.68		
Uric acid (commercial)	By Dumas 33.0	32.86	32.87	33.2	
		32.94	32.83	33.2	
		33.05	Av. 32.85	Av. 33.2	
		32.87			
		Av. 32.93			
Acetanilide	10.37	10.17	10.31		
		10.34	10.21		
		Av. 10.26	Av. 10.26		
Metol, recryst.	8.19		8.14		
			8.18		
			Av. 8.16		
Amyl-*p*-toluidine–hydrochloride (Cl = 16.59%; calc. 16.60%)	6.56		6.55		
			6.56		
			Av. 6.56		
p-Nitrophenol (zinc reduction)	10.08		10.08		
			10.09		
			10.14		
			Av. 10.10		

[a] Used 25 cc. sulfuric acid, $CuSO_4$-$HgSO_4$ catalyst, 10 grams sodium sulfate; digestion about 1 hour after clearing.
[b] Used Pregl procedure for digestion, with selenium catalyst. Results rounded off to three significant figures.

by a half-drop overtitration; (2) the end point is visible by daylight or by ordinary electric light, making available the advantages of boric acid absorption without need for special light equipment; (3) the color-matching titration can be used equally well in the macro- and the micro-Kjeldahl methods.

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Flask Oxidation in the Determination of Sulfurous Acid by Distillation

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In the determination of sulfurous acid by distillation from dried fruits and other products two difficulties have long been recognized. First, some of the sulfurous acid may be oxidized before it reaches the receiver. Second, especially in volumetric methods, reducing substances other than sulfurous acid may react in the receiver and give too high results. Among the means that have been recommended or adopted to overcome the first difficulty are steam distillation, distillation in a stream of carbon dioxide, rapid boiling, and the addition of sodium bicarbonate together with extra acid to the sample before distillation. Among the means used for overcoming the second difficulty are the substitution of iodine for bromine in the receiver, the use of gravimetric methods, the benzidine gravimetric method, and the use of cold hydrogen peroxide as a selective oxidant.

In a previous paper (*2*) the authors have reported a study of some phases of the problem, in which dried fruits and other products were used, and a few observations with sulfurous acid solutions made by passing sulfur dioxide gas from a cylinder through distilled water were included. When the available methods are used the true sulfurous acid content of dried fruit samples is to some extent uncertain. No entirely satisfactory reference substance has been found. In the authors' experience sulfurous acid solutions were less susceptible to oxidation and hence more satisfactory than solutions of sulfites or bisulfites.

In the study previously reported (*2*) the authors employed a type of distillation apparatus that lends itself well to the investigation of several of the means suggested for preventing oxidation in the distillation flask under closely comparable conditions. Such an investigation has been made upon sulfurous acid solutions, and the results are shown in Table I. Except in the two cases noted, the solutions were made by passing sulfur dioxide gas from a cylinder into ordinary dis-

Table I. Determination of Sulfurous Acid

Experiment	Method	SO_2 Added	Total Acid as SO_2	Recovered in Distillate[a] Volumetric method	Recovered in Distillate[a] Gravimetric method	SO_4 in Distilling Flask as SO_2 Original	SO_4 in Distilling Flask as SO_2 Found	Total S Accounted for as SO_2[b]
		Gram	*Gram*	%	%	*Gram*	*Gram*	%
1	$HCl + NaHCO_3$[c]	0.0346	0.0424	76.9 ± 2.0	.....	0.0078	0.0158	100.0 ± 1.2
2	$HCl + NaHCO_3$	0.0369	0.0368	95.7 ± 0.0	.....	0.0001	0.00005	96.0 ± 0.0
3	$HCl + NaHCO_3$[d]	0.0362	0.0444	88.4 ± 0.5	.....	0.0082	0.0086	91.2 ± 7.8
4	$HCl + NaHCO_3$. Vent closed	0.0369	0.0368	94.9 ± 0.0	.....	0.0001	0.00035	96.1 ± 0.0
5	$HCl + NaHCO_3$. No vent	0.0369	0.0368	80.7 ± 3.9	.....	0.0001	0.0064	98.3 ± 0.9
6	$HCl + NaHCO_3$. Air stream	0.0367	0.0404	93.2 ± 0.8	.....	0.0037	0.0039	94.5 ± 1.1
7	$HCl + NaHCO_3$. CO_2 stream	0.0367	0.0404	94.8 ± 1.7	.....	0.0037	0.0029	93.1 ± 1.4
8	HCl but no $NaHCO_3$	0.0369	0.0368	96.8 ± 0.7	.....	0.0001	0.0000	97.0 ± 0.7
9	$H_3PO_4 + NaHCO_3$. Distilled into H_2O_2	0.0391	0.0411	.....	70.8 ± 3.9	0.0020	0.0120	96.6 ± 4.7
10	$HCl + NaHCO_3$. Distilled into H_2O_2	0.0400	0.0414	73.0 ± 0.8	71.0 ± 0.8	0.0014	0.0122	98.1 ± 0.8[e]
11	Monier-Williams	0.0367	0.0404	85.9 ± 0.1	99.2 ± 0.3	0.0037	0.0002	100.0 ± 1.2[f] 78.3 ± 0.3[f] 90.5 ± 0.5[e]
12	Monier-Williams. No preliminary heating	0.0367	0.0404	88.7 ± 0.3	98.6 ± 0.2	0.0037	0.0001	80.8 ± 0.1[f] 89.8 ± 0.1[e]
13	Monier-Williams. No preliminary heating; no guard trap	0.0400	0.0414	88.0 ± 0.2	93.5 ± 1.4	0.0014	0.0000	85.0 ± 0.2[f] 90.3 ± 1.3[e]

[a] Referred to third column.
[b] Referred to fourth column.
[c] Sulfurous acid solution in tap water.
[d] Sulfurous acid solution in recently boiled distilled water.
[e] Based on gravimetric determination of SO_2 in distillate.
[f] Based on volumetric determination of SO_2 in distillate.

tilled water. Thiosulfate guard traps were used in experiments 6 and 7.

Included in the table are also observations on certain modifications of the method suggested by Monier-Williams (*1*). The modifications include omission of the preliminary heating of the acidified water (experiment 12), the elimination of the guard trap (experiment 13), and the direct rather than reflux distillation of the sulfurous acid into cold hydrogen peroxide without use of the carbon dioxide stream (experiments 9 and 10).

In all cases where the filtered residue after distillation gave a perceptible precipitate with barium chloride, the amount was determined gravimetrically.

The concentration of sulfurous acid in the initial solutions used was determined by titration into iodine checked against 0.1 *N* sodium thiosulfate. The total acid was determined by 0.1 *N* alkali titration after oxidation of the sulfurous acid by neutral hydrogen peroxide, and was calculated as sulfur dioxide. The difference between this value and that obtained by titration into iodine was considered as the amount originally present as sulfate. In calculating the per cent recovery of sulfurous acid in the distillate, the basis for calculation was the value obtained for the original solution by iodine titration. In calculating the per cent recovery of total sulfur—that is, the sum of the recoveries in distillate and distilled residue—the basis was the alkalimetric titration of the oxidized original solution.

Discussion

When the Monier-Williams method (experiment 11) and modifications of it were used, the recovery in the distillate by the gravimetric method was higher than that by the volumetric (alkali titration). That this does not necessarily occur when hydrogen peroxide is used as the oxidant is shown by experiment 10 in which both volumetric and gravimetric determinations were made with the regular apparatus, not using a reflux condenser. This also seems to indicate that no appreciable amount of hydrochloric acid was distilled over when no reflux condenser was used.

From the averages of the probable errors of the means, given in Table I, it appears that the accuracy of the volumetric determinations of sulfurous acid in the distillates by volumetric methods was slightly less than 1 per cent; the accuracy of gravimetric determinations was approximately 1.3 per cent; and the accuracy for the total recovery was 1.5 per cent by volumetric and 1.6 per cent by gravimetric methods. The results therefore appear dependable to the nearest milligram of sulfur dioxide. Considering the highest values obtained for the distillate, whether volumetric or gravimetric, low recoveries of sulfurous acid in the distillate were generally accompanied by increased yields of sulfate in the distilled residue.

So far the results indicate that when low values were obtained in the distillate, oxidation in the distilling flask was appreciable (experiments 1, 5, 9, and 10). However, it is not clear why such oxidation and low sulfurous acid recovery in the distillate did not take place in other experiments. For example, oxidation apparently occurred in experiment 10, but not in experiment 2. These experiments differ only in that the oxidants used were different, and there is no reason to suppose that this would influence oxidation in the distilling flask.

No advantage appears to result from the use of recently boiled distilled water either for making up the sulfurous acid solutions or in the distillation flask (experiments 2, 3, 11, and 12). The use of tap water in making up the sulfurous acid solution resulted in a lower yield (experiments 1 and 2).

No advantage resulted from using a carbon dioxide stream during distillation (experiments 2 and 7), and the use of an air stream in the distillation flask did not accelerate oxidation (experiments 2 and 6). This is further indicated by a comparison of experiments 2, 4, and 5. Removal of the vent tube (experiment 5) should hasten the elimination of air from the flask as compared with using a vent tube closed off at the top (experiment 4) or using a vent tube open at top and bottom (experiment 2), but this did not increase the yield of sulfurous acid. No explanation is offered for the greater apparent oxidation that occurred when the vent tube was removed altogether (experiment 5).

The use of sodium bicarbonate did not increase the yield from sulfurous acid solutions.

Summary

None of the various means that have been suggested for preventing flask oxidation and increasing the yield in the determination of sulfurous acid proved to solve the problem in the authors' experiments.

Gravimetric determinations by the Monier-Williams method gave the highest yields, and it appeared that the preliminary heating could be omitted without serious loss of accuracy.

Among volumetric methods, that of Nichols and Reed, but with the omission of sodium bicarbonate, gave the highest results.

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"That which is brief, if it be good, is good twice over."

Mold Growth Test for Minute Amounts of Arsenic

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THE unusual property of certain mold growths in liberating arsenic in the form of gas having a characteristic garlic-like odor was clearly demonstrated in a series of experiments reported by Gosio in 1892 (*3*), and has been studied by many other investigators. A recent contribution by Thom and Raper (*7*) shows the particular molds that have this property and also gives references to the literature on the subject. Tanner (*5*) gives the method developed by Schneider (*4*) for using these molds in testing for the presence of arsenic. Challenger et al. (*1*) examined the gas evolved and found it to be trimethyl arsine. They give data as to the gas itself and certain of its compounds.

The present work gives some convenient ways for growing the mold, suggests methods for carrying out the test for arsenic in food products, records the results obtained with known amounts of arsenic in different kinds of foods, shows that many classes of arsenic compounds respond to the test, and points out certain limitations.

The authors believe that this mold test for arsenic has a value that is not generally appreciated by those interested in food technology. It provides a presumptive test materially more sensitive than existing chemical tests. It should have marked qualitative value in supplementing chemical quantitative tests where large numbers of samples of unknown arsenic content are to be tested. The production of mold growth and method of treatment are procedures that could be reduced to practical simplicity in routine examination.

In this work only one kind of mold was used—namely, *Scopulariopsis brevicaulis* (*Sacc.*) *Bainier*. This appears in the older literature as *Penicillum brevicaule Sacc.* It is described in detail by Thom (*6*) and the particular strain used is listed in his collection as No. 480.2. The authors are indebted to Doctor Thom for the original spores of this mold and for many helpful suggestions about the work here reported.

The mold grows freely on many kinds of food materials, as well as in the usual culture solutions. Tomato broth, pea broth, shrimp meat, potted meat, and apple pomace were observed to support vigorous growths. In order to simplify and standardize the tests a synthetic medium, Czapek's solution with agar, was used. This medium is easily prepared from usual laboratory reagents that are free from arsenic. Because many bacteria do not grow well in this medium the harmful effects of this type of contamination are minimized.

Czapek's Solution Agar

Water	1000 cc.
	Grams
Sodium nitrate	3
Potassium monohydrogen phosphate	1.0
Magnesium sulfate	0.5
Potassium chloride	0.5
Sucrose	30.0
Agar agar	15.0

If arsenic is present in the media on which this mold is grown, the gaseous arsenic compound which may be detected by its characteristic garlic-like odor is given off. But a more satisfactory way to conduct the test, originally established by Gosio (*3*), involves the cultivation of a vigorous growth of the mold on the surface of a solid or semisolid arsenic-free medium in separate containers and subsequent addition of the sample to the surface of the mat of mold mycelium. Less than 0.001 mg. of arsenic will give a definite odor in 2 hours under the conditions described.

Experimental

Short wide tubes and also Petri dishes were used to give a large surface of agar media on which to grow the mold. A thin layer of melted media was poured into the sterile Petri dishes and allowed to solidify. The melted medium in the sterile tubes was cooled with the tubes inclined to give slants with the maximum surface. A few drops of a suspension of the mold spores in sterile water were spread over the surface of the solid media in the dishes and in the tubes. Tests showed that the mold grows best at about 30° C. Incubation of the inoculated media at 30° C. produced a vigorous growth of mycelium in 48 to 72 hours.

Experiments showed that the first noticeable growth of mold is able to generate the test gas, but more complete growth gives the test more quickly and with a smaller amount of arsenic. A thick mat of white mycelium gives best results. After spore formation has become general, as shown by the brownish color over most of the surface of the mold, the reaction is less definite. The generation of the test gas by the action of the mold on the sample takes place at least as well at room temperature as in the incubator at 37° C.

The sample may be in the form of a dry powder or a liquid. The test gas seems to be evolved as a product of respiration of the growing mycelium in contact with the sample. The arsenic in the sample is apparently dissolved by moisture on the surface of the mycelium and the test gas seems to be given off from the surface of the mold. In order to make possible the greatest amount of contact of the sample with the mold, the dry sample should be ground coarsely and sprinkled evenly over the surface of the mold. If the sample is in liquid form not more than 1 cc. should be used. It was at first thought that a liquid sample would be better because of more complete contact with the mold, but the first experiments showed that a small amount of arsenic finely divided with inert material such as sand gave as good a test as the same amount of arsenic in liquid form.

Since the test depends on the development of arsenic vapor sufficiently concentrated to detect by the odor, the amount of gas space confined above the mold during the test is important. The relation of the area of actively growing mold to the volume of gas in the test apparatus will influence the concentration of the test gas developed from the arsenic present. Thus Petri dishes gave a better test than stoppered tubes because the relation of mold area to air space was greater. Moreover, by gently tilting the cover of the Petri dish at one side the gas may be readily detected.

It was possible to obtain a definitely positive test in 2 hours with only 0.5 microgram of arsenic trioxide present, either dried on 1 gram of sand or dissolved in 1 cc. of water. This is equivalent to 1 part in 2 million or 0.00005 per cent. The actual weight of arsenic in the gas mixture that gives a distinct odor must be exceedingly small, because only a small portion of the dry sample can come into actual contact with the mold and the gas continues to be given off for several hours. Using 100 micrograms of arsenic trioxide on sand a definite odor was obtained in 20 minutes.

Different kinds of food products were tested with and without added arsenic. Products which could be dried were coarsely ground and used directly on the mold. Large amounts of fat in meat products delayed for several hours the formation of sufficient gas to give the test. This delay was avoided by preliminary extraction with ether and alcohol followed by drying and grinding of the sample. Fine powders such as flour formed a cake which interfered with the contact with the mold. This was overcome by adding a little calcium carbonate, ashing, neutralizing with hydrochloric acid and using either the solution or the residue after evaporation to dryness. This ashing procedure is also advantageous with samples that have a strong odor that might confuse the test. In all these tests 1 microgram of arsenic trioxide in 1 gram of sample was easily detected.

As has been reported elsewhere (*7*), the nature of the arsenic compound that may be present does not seem to affect the test. Five kinds of arsenic compounds were tested to indicate its general applicability. With each compound, an amount of sample equivalent to 1 microgram of arsenic trioxide gave a definite test in 2 hours.

1. Arsenous oxide, an insoluble white arsenic powder.
2. Sodium arsenite, a simple soluble compound.
3. Paris green, a complex metallic compound.
4. Sodium cacodylate, a very stable arsenic radical.
5. Neosalvarsan, a highly complex organic compound.

The presence of fruit acid in reasonable amounts does not prevent the test. One per cent citric acid either dry-mixed with the sample or in solution with the sample did not interfere. One per cent sodium carbonate in solution with the sample prevented the test with small amounts of arsenic. Larger amounts of arsenic gave a delayed test. One per cent sodium carbonate dry, mixed with the powdered sample, made the test less satisfactory. Small amounts of ammonium hydroxide, enough to give a perceptible odor, did not obscure the test.

The presence of inorganic mercury compounds completely prevents the test. The gas that is formed combines easily with mercury to form stable compounds (*1*, *4*). Mercury through its toxicity may also paralyze the respiratory mechanism and thus prevent production of the test gas. Antimony compounds to not interfere. One hundred micrograms of antimony chloride gave no test. Selenium and tellurium compounds give gases similar to those of arsenic, but these elements are very rare (*7*).

Attempts were made to gain an insight into the mechanism by which the test gas is formed. Enzymes were produced by the method described by Dox (*2*) and were tested with arsenic-containing substrates. Results were uniformly negative, and even though no claim for exhaustive treatment is made this fact is regarded as significant in indicating that the gas production is intimately associated with the active mold growth. Also supporting this viewpoint are the following observations:

When plates showing vigorous growth were thoroughly cooled by subjecting to ice box temperature for 30 minutes, 20 micrograms of arsenic trioxide failed to give a positive test in 2 hours' continued exposure to that temperature.

When normal growth was inhibited by covering the mold mat with distilled water 100 micrograms of arsenic trioxide applied with sand failed to present a positive test in 30 minutes, 1 hour, 5 hours, and 30 hours, whereas the control dish without water gave a strong test in 20 minutes.

Quicker reactions were observed when the test substance was applied to actively growing mold rather than one in which sporulation had progressed to an advanced degree.

Recommended Procedure

The following is suggested as a workable procedure that will apply to a wide classification of food products:

1. Prepare and sterilize Czapek's solution agar. This may be prepared in large quantities and held in stock.
2. Sterilize Petri dishes and, using precaution against contamination, introduce thin layers of Czapek's medium after previously liquefying by heat.
3. Allow the medium to harden in the Petri dishes. Inoculate with a spore suspension in water by dropping 3 or 4 drops on the surface of the medium and, by tilting the plates, cover the surface as completely as possible. The spore suspension is prepared by flooding the surface of an old slant culture with 5 cc. of sterile water and scraping the spores into the water by means of a sterile platinum needle or pipet. Slants are prepared by the usual bacteriological method, using Czapek's agar. They may be made in large quantities and the inoculated slants held in stock.
4. Incubate the plates 48 to 72 hours at 30° C. or at lower temperatures, until an obviously active growth covers the inoculated portion of the plate.
5. Prepare the test substance by one of the following methods:

Solid Materials. Wherever practicable dry, if necessary, and grind to a coarse powder.

If the product is distinctly oily, extract with two or three portions of ether or chloroform by stirring and decantation. Dry if necessary, and grind to a coarse powder.

If the product is a very fine powder such as flour, add an excess of sodium or calcium carbonate, char completely, acidify with dilute hydrochloric acid, filter, and test the filtrate as directed below.

If the product has a strong odor, char and extract as described above.

Liquid Materials. Adjust the acidity with dilute acid or alkali until the solution is barely acid to litmus. Concentrate by evaporation if desirable.

6. Apply the sample to the mold growth:

Using the prepared solid sample material, sprinkle about 1 gram fairly evenly over the mold surface.

Using the prepared liquid sample, transfer about 1 cc. to the surface of the mold growth. The liquid stays in large drops which may be better distributed by first sprinkling on a few grains of clean sand. Shake the dish to spread the liquid somewhat, but it is not desirable to cover the entire surface of the mold growth.

7. Allow to remain at room temperature in a room free from pronounced odors. Test for the characteristic odor in 0.5, 1, 2, and 5 hours. If small amounts (0.000001 gram) of arsenic are present, the odor should be apparent in 2 to 5 hours. A quicker reaction will indicate the presence of larger amounts. Consider the test negative after 16 to 20 hours without the characteristic reaction.

Summary

Analysts are sometimes called on to test a small sample for possible traces of arsenic. Even the Gutzeit test is not satisfactory with only 1 or 2 micrograms of arsenic present. This mold test may be used with 1 gram or less of sample and detects easily one part per million of arsenic.

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An Accurate Semimicro-Kjeldahl Method

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DESCRIPTIONS of the determination of nitrogen by the Kjeldahl method and its modifications usually include no estimate of the accuracy of the results. In the exceptionally careful work of Andersen and Jensen (*1*), results accurate to 0.1 or 0.2 per cent were obtained after long periods of digestion, 4 to 8 hours. Although much faster micromethods have been described, Peters and Van Slyke (*12*) advise the use of macromethods if the error is to be kept under 1 per cent. Northrop (*8*) has used a semi-micromethod with an accuracy of 0.2 per cent. The authors have modified his method by the use of mercury and selenium together as catalysts, having confirmed the finding of Osborn and Krasnitz (*9*) and of Taylor (*14*) that the combined catalysts work faster than either alone.

Method

Five-cc. samples of solution, containing 5 to 6 mg. of nitrogen, were pipetted into 100-cc. Pyrex Kjeldahl flasks having a constriction about halfway up the neck (*8*). After the addition of 2 cc. of concentrated sulfuric acid, 1 gram of potassium sulfate, 70 mg. of mercuric oxide, and 2 drops of selenium oxychloride, together with a few pieces of broken alundum to minimize bumping, the digestion was carried out over microburners, the flasks being protected from superheating by asbestos board having a 2-cm. hole under each flask. The time required to drive off the water was about 20 minutes, the mixtures became clear in 6 to 8 minutes more, and digestion was continued for 20 minutes after clearing. After adding 35 cc. of water and 5 cc. of a solution composed of 500 grams of sodium hydroxide, 500 cc. of water, and 80 grams of anhydrous sodium thiosulfate, the ammonia was distilled through 2 traps fused together in series (*8*) and a Pyrex condenser into 25 cc. of 0.02 *N* hydrochloric acid. Distillation was continued until violent bumping occurred, the time required being about 20 minutes and the volume of the distillate being about 25 cc. The excess acid was titrated with 0.02 *N* sodium hydroxide, using methyl red as indicator. Blank determinations were carried out with 5 cc. of water, digested and distilled in exactly the same way.

Results

Analyses were run in quadruplicate, the titrations usually agreeing within 0.1 cc. of a 0.02 *N* solution, the average deviation from the mean of individual titrations in a set of 4 being 0.02 to 0.03 cc. Blank titrations varied from 0.05 to 0.15 cc. with different lots of distilled water, the average deviation of any set of 4 being 0.01 to 0.02 cc. Since the ammonia amounted to about 20 cc. of a 0.02 *N* solution, a liberal estimate of the mean error, considering only the agreement of duplicates, would be 0.2 per cent.

The weight of pure nitrogenous substance in each 5-cc. sample analyzed was known to within 0.1 per cent, as samples of 0.6 to 1.4 grams were weighed, dissolved, and diluted to 100 cc. The concentrations given are based on dry weight determinations of 1-gram samples which were dried *in vacuo* to constant weight in 1 to 2 days at 75° C. in an Abderhalden drier containing anhydrous magnesium perchlorate (Anhydrone) in the bulb.

The materials analyzed were tyrosine, glycine, edestin, casein, and egg albumin. The tyrosine was prepared from casein and purified by three recrystallizations from water, as previously described (*4*). The glycine solution was prepared by Owen (*3*, *11*), and its concentration is based on his dry weight determinations. Edestin was prepared from hemp seed according to Osborne, recrystallized, and washed free from salt, as described elsewhere (*5*). The casein was Casein II, described in a previous paper (*6*). The egg albumin was prepared by a method developed by Cannan (*2*) involving crystallization from sodium sulfate solutions. It was twice recrystallized, and freed from salt by dialysis until a 7 per cent solution had a specific conductivity of 1.1×10^{-4}. Its concentration was determined by evaporating 10-gram samples of solution at 50° C. and drying at 75° C. as described. Another 10-gram sample of this solution was diluted to 100 cc., and 5-cc. samples of the dilute solution were analyzed.

Table I. Determination of Nitrogen in Amino Acids and Proteins

Substance	Substance in Sample	Nitrogen Found		Accepted Value	Source of Accepted Value
	Mg.	*Mg.*	%	%	
Tyrosine	70.57	5.45	7.72	7.735	Formula
Glycine	36.65	6.84	18.66	18.67	Formula
Edestin	28.02	5.22	18.63	18.69	Osborne (*10*)
Casein	34.45	5.34	15.50	15.49	Authors' macro
Egg albumin	35.09	5.47	15.59	15.64	Sörensen (*13*)

In the case of the two amino acids, the results check the theoretical within 2 parts in 1000. In the case of edestin and egg albumin, the results are 3 parts in 1000 lower than figures selected as the most reliable in the literature. For casein the values in the literature vary from 15.4 to 15.8 per cent. Since Linderström-Lang (*7*) has shown casein to be a mixture, such variations in different preparations are to be expected. Accordingly, the authors have compared their result with one obtained with the same casein solution, using a macromethod and a digestion period of more than 4 hours.

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Direct Titration of Sulfate

Tetrahydroxyquinone as an Internal Indicator

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ALMOST none of the methods suggested for the rapid determination of the sulfate content of a solution make possible direct titration without recourse to the use of outside indicators, a back-titration, or a filtration. The tetrahydroxyquinone method described in the present paper makes it possible to titrate the sulfate present in a sample directly with a standard barium chloride solution. The end point is indicated by the appearance of the red barium salt of tetrahydroxyquinone.

The present study was made possible through the financial support of the Joint Research Committee on Boiler Feedwater Studies, and, naturally, a large share of emphasis in the development of the method has been placed on making it applicable to the analysis of boiler waters. The concentration ranges considered and the effect of various impurities which were studied are those which might be expected in boiler water analysis. The actual application should, however, by no means be limited to any one particular field, and with proper preliminary investigation the method may be widely useful.

Review of the Literature

The gravimetric method for the determination of sulfate is very accurate and, except where occlusion and adsorption errors are high, is free from serious interference. It has the disadvantage of being time-consuming and of requiring the use of a balance, which is not always available for routine analysis. For these reasons methods which were essentially gravimetric were not considered in the present investigation.

Several methods which might be classified as colorimetric have been suggested for the determination of sulfate (*41, 59, 69, 99, 116–118*). Most of them, while perhaps satisfactory in laboratory work, are too complicated for routine analysis.

The methods suggested in the literature as suitable for the rapid determination of sulfate may be roughly divided into three classes: first, filtration methods; second, those determinations in which a titration is used, with internal or external indicators; and third, turbidimetric methods.

Filtration Methods. The benzidine method is probably the best known example of a filtration method. It has been the subject of extensive investigation (*16, 20, 49, 84, 109*) and the concentrations of impurities (*16, 17, 20, 37, 56, 91, 105, 109*), concentrations of reagents (*17*), temperature and method of titration (*31, 37, 46, 57, 90, 95, 105*), and the method of filtration and washing (*31, 95, 119*) have all been carefully studied.

Carbonate salts are also often used (*9, 11, 23, 34, 53, 83, 108*). For example, to a solution containing sulfate a standard barium chloride solution may be added, followed by sodium carbonate; after filtering off the barium carbonate and sulfate precipitated, the carbonate in either the filtrate or precipitate may be determined by a titration and from this the sulfate can be calculated. Chromate (*1, 12, 13, 15, 29, 39, 50, 51, 61, 63, 68, 72, 75, 81, 92, 94, 97, 100, 102, 111*), phosphate (*74*), lead (*36, 85*), and oxalate salts (*93*) are often used in a somewhat similar manner.

In another method, which does not involve a filtration but which depends on a partial separation of the solution and solid, the solution is centrifuged and the volume of the precipitate measured (*3, 4, 44, 71*). Where a centrifuge is available this method is sometimes satisfactory for the routine determination of sulfate.

All these procedures demand a filtration, which necessarily makes the method rather long. Direct titration methods would have considerable advantage in regard to the speed with which a determination could be made.

Titration Methods. Several methods which have been worked out for the titration of sulfate depend on the use of lead salts (*40, 58, 78, 82, 85*). In general, however, the lead sulfate which is precipitated is too soluble to make these methods readily applicable in dilute solutions.

Three methods are available for the determination of sulfate in which outside indicators are used to determine the end point. The indicators used are starch–potassium iodide paper (*18*), congo red and ammonium dichromate (*110*), and benzidine paper (*30*). Other methods use chromate salts for the titrating solution and various indicators (*38, 96, 113, 114*). For routine analysis the use of outside indicators is too slow and subjects the method to inaccuracies.

Several titration methods use internal indicators. One series depends on the hydrolysis of a salt of a strong base and a weak acid to indicate the end point—for example, a method which adds excess barium chloride and titrates the excess barium with sodium carbonate in the presence of phenolphthalein. When all the barium has been precipitated as barium carbonate, the addition of a slight excess of sodium carbonate will cause the phenolphthalein to turn pink (*19, 22, 101*). A number of salts, such as sodium carbonate, potassium chromate (*7, 14, 45, 57, 104*), potassium stearate (*5*), or potassium palmitate (*6, 60, 120*), have been used in this titration.

In many cases titration methods which depend on hydrolysis reactions are satisfactory. They are, however, subject to interference from the presence of phosphate and carbonate, and to some extent from other buffer salts, such as silicates and aluminates.

Some titration methods have been evolved which depend on the use of adsorption indicators (*8, 112*).

Another internal indicator method titrates with potassium chromate to the end point of silver chromate (*70*), but is, of course, subject to interference by chloride. Other titration methods depend on conductivity measurements (*32, 35, 55, 64, 66, 77, 80*), thermometric measurements (*25, 33*), refractometer measurements (*10*), and various other means of determining the end point, but are not in the main readily applicable to routine analysis.

An internal indicator method which seems to be convenient and rapid has been worked out recently in Germany (*65, 89, 103*). This adds excess standard barium chloride and titrates back with standard sodium sulfate in the presence of a rhodizonate salt. It will be considered further in the discussion of the tetrahydroxyquinone method.

Turbidimetric Methods. Several rather different methods have been suggested as being applicable to the turbidimetric determination of sulfate. One compares the turbidity of the unknown solution with a known solution (*2, 21, 24, 26–28, 62, 67, 73*). A second measures the time required for a solution to become turbid after the precipitating agent has been added (*115*). The third, which is most used at the present time, measures the depth of turbid liquid required to obscure a light filament (*43, 47, 87, 88*).

Much study has been devoted to the method based on the measurement of the depth of liquid required to obscure the light filament. Various ways of adding the barium chloride used in the precipitation have been tried (*47, 54, 76, 79, 106*), and the effect of various salts, the effect of temperature, method, and time of addition of acid and various other reagents, and the acid concentration of the sample during precipitation (*48, 54, 76, 79, 86, 87, 106*) have all been extensively investigated.

The accuracy of the turbidimetric methods has been the subject of much discussion (*48, 54, 86*). In general investigators are not in good agreement as to accuracy.

The turbidimetric method for the determination of sulfate has found wide application and in many instances is entirely

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satisfactory. Its chief disadvantages are: As ordinarily carried out the method requires the construction of a calibration curve; some special equipment aside from the regular analytical equipment is necessary; the range of concentrations over which the method may be used is quite short; the method is considerably influenced by other salts in the solution; and its accuracy in some instances is subject to considerable doubt.

It is evident that the benzidine method, the hydrolysis methods, and the turbidimetric methods should prove of considerable value in the determination of sulfate. In the present investigation the benzidine method and the turbidimetric methods were extensively studied, but the results will not be discussed here. Because of the particular solutions in which the authors were interested the hydrolysis methods did not seem satisfactory and were not considered in detail.

The rhodizonic acid method (*89*, *103*) seemed to promise a very satisfactory method for the rapid determination of sulfate and offered considerable improvement in many respects over the three methods mentioned. For this reason it was investigated further and this investigation will be considered briefly below.

Investigation of Tetrahydroxyquinone Method

In 1929 Strebinger and Zombory (*103*) suggested the use of rhodizonic acid in the titration of sulfate. The determination was carried out by the addition of an excess of standard barium chloride to the sample, followed by the addition of a small amount of the sodium salt of rhodizonic acid. The excess barium was titrated back with a standard sodium sulfate solution. The addition of the barium chloride caused the precipitation of the sulfate and also of the barium salt of rhodizonic acid. This salt has a bright red color which is readily distinguished in the solution. On back-titration with sodium sulfate the barium salt of rhodizonic acid is destroyed because of the precipitation of barium sulfate, and the end point is denoted by the disappearance of the red color. If the titration is being carried out in a neutral solution, the rhodizonate salt goes back into solution to form the sodium salt and the end point is a change from red to yellow. If the titration is being carried out in an acid solution, the rhodizonate salt is destroyed and the end point is a change from red to colorless. The barium salt of rhodizonic acid is quite stable in a dilute acid solution.

In the present study the use of rhodizonic acid was investigated. In solutions about 0.1 or 0.2 *N* with respect to sulfate the method was found satisfactory, although the results obtained were not as accurate as those obtained by Strebinger and Zombory. The method was not found satisfactory on more dilute solutions. It was also impossible to use rhodizonic acid as indicator in the direct titration of sulfate with barium chloride. Some of the rhodizonic acid used in this investigation was secured from Germany and some was prepared in the laboratory.

Tetrahydroxyquinone is used in a similar manner to rhodizonic acid and gives the same end-point reactions. It is, however, more satisfactory in dilute solutions and can be used in the direct titration.

Results of Back-Titration. In making rhodizonic acid it was necessary as one of the preliminary steps to prepare some tetrahydroxyquinone. Its use as a qualitative indicator for barium has been noted (*42*), and a few preliminary experiments indicated that it might be used in a quantitative determination.

The tetrahydroxyquinone was made by treating glyoxal sodium bisulfite, prepared by treatment of acetaldehyde with nitric acid and sodium bisulfite (*107*), with a solution of sodium carbonate (*52*). Solutions of tetrahydroxyquinone in water are not sufficiently stable to be added to the sample in this form. It is also inconvenient to make up fresh solutions of the indicator every time it is desired to use it. It has been found very satisfactory to grind up a small amount of the indicator with a large amount of potassium chloride and add a few tenths of a gram of this mixture to the sample to be analyzed. In this form the indicator is stable for a year or longer. This method of adding the tetrahydroxyquinone to the sample was used throughout the present investigation.

A few preliminary results for the back-titration involving the titration of solutions of barium chloride with potassium sulfate are shown in Table I. The results, as seen, are satisfactory. In this titration it was found desirable to have alcohol present in the sample, since this hastened the precipitation of the barium sulfate.

Table I. Titration of Barium Chloride with Potassium Sulfate

Sample	$BaCl_2$ Solution	$BaCl_2$ Corrected to 0.05 *N*	K_2SO_4 0.05 *N*
	Cc.	*Cc.*	*Cc.*
1	1.00	1.98	2.03
2	1.00	1.98	2.05
3	5.00	9.90	9.95
4	5.00	9.90	9.90
5	10.00	19.80	19.75
6	10.00	19.80	19.70

50-cc. samples with 15 cc. of alcohol added.
Solutions approximately 0.03 *N* with respect to hydrochloric acid.
$BaCl_2$ solution 0.1 *N*. Correction factor = 0.990.

The effect of acid concentration, temperature, and various other ions on this back-titration was studied. The solution to be titrated should be kept below 0.05 *N* with respect to hydrochloric acid. The temperature should also be below 30° C. Hydroxide, chloride, carbonate, silicate, calcium, magnesium, and aluminum do not interfere unless they are present in high concentrations. If the sample is made sufficiently acid during the addition of the barium chloride and then this acidity is neutralized before the back-titration with sodium sulfate, fairly high concentrations of phosphate may be present without causing interference. Iron present in the sample causes interference and must be removed.

Results of Direct Titration. In the direct titration the sample to be analyzed is neutralized and then titrated directly with a standard barium chloride solution to the appearance of the red color of the precipitate of the barium salt of tetrahydroxyquinone. During the present investigation an approximately 0.025 *N* barium chloride solution was used in all the titrations. A fairly high concentration of alcohol in the sample was also found very desirable during the titration.

Table II. Analysis of Sodium Sulfate Solutions by Direct Titration Method

Sample	$BaCl_2$ Used	SO_4 Present	SO_4 Found
	Cc.	*Mg.*	*Mg.*
2	4.2	5.00	5.02
3	6.2	7.50	7.48
4	8.2	10.00	9.92
1	10.1	12.50	12.2
5	14.4	17.50	17.5
6	16.2	20.00	19.7
7	19.8	25.00	24.2

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol added.
Blank = 0.1 cc.

In Table II are shown the results of a few preliminary titrations by the direct method on solutions containing only sodium sulfate. The results are satisfactory. It will be noticed that for samples containing more than 20 mg. of sulfate in the 25 cc. of solution titrated there is some tendency toward low results. This was confirmed by further investigation, and in order to avoid this error it seems best to keep the concentration of sulfate below 20 mg., using not more than 16 or 17 cc. of the 0.025 *N* barium chloride solution in a titration. The 0.1-cc. blank indicated in this table is the amount of

barium chloride required to give a visible precipitate with the indicator when no sulfate is present.

The effect of various ions on the direct titration is shown in Table III. Carbonate, aluminum, silicate, and magnesium have little effect. Carbonate and aluminum in concentrations higher than those shown in the table tend to make the end point slightly less sharp.

Table III. Effect of Various Ions on Direct Titration

Sample	Added Ion		$BaCl_2$ Used	SO_4 Present	SO_4 Found
		Mg.	*Cc.*	*Mg.*	*Mg.*
12	CO_3	4.0	2.10	2.50	2.45
13	CO_3	4.0	6.3	7.50	7.60
14	CO_3	4.0	12.3	15.00	14.9
8	CO_3	8.0	4.2	5.00	5.02
9	CO_3	8.0	10.4	12.50	12.6
10	CO_3	8.0	16.6	20.00	20.2
11	CO_3	8.0	20.2	25.00	24.6
20	Al	2.5	2.30	2.50	2.70
21	Al	2.5	6.2	7.50	7.47
22	Al	2.5	12.2	15.00	14.8
23	Al	5.0	2.30	2.50	2.70
24	Al	5.0	6.5	7.50	7.83
25	Al	5.0	12.2	15.00	14.8
28	SiO_3	5.1	2.20	2.50	2.57
29	SiO_3	5.1	6.3	7.50	7.60
30	SiO_3	15.3	2.20	2.50	2.57
31	SiO_3	15.3	6.2	7.50	7.47
32	SiO_3	25.5	2.15	2.50	2.51
33	SiO_3	25.5	6.2	7.50	7.47
34	SiO_3	25.5	12.3	15.00	14.9
39	Mg	2	2.30	2.50	2.70
40	Mg	4	6.1	7.50	7.35
41	Mg	10	12.2	15.00	14.8
35	Ca	5.0	2.10	2.50	2.45
37	Ca	0.25	6.1	7.50	7.35
38	Ca	0.50	6.4	7.50	7.70
15	PO_4	0.9	2.30	2.50	2.45
16	PO_4	0.9	6.5	7.50	7.60
17	PO_4	1.7	2.80	2.50	2.70
18	PO_4	1.7	7.0	7.50	7.83
19	PO_4	1.7	12.9	15.00	15.1

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol.
Blank, 0–0.6 mg. PO_4 = 0.1 cc.
0.6–1.2 mg. PO_4 = 0.3 cc.
1.2–1.8 mg. PO_4 = 0.6 cc.

Table IV shows the results of the direct titration on solutions containing several ions. These samples were all made up with sodium salts of the various ions shown.

Table IV. Direct Titration of Samples Containing Hydroxide, Chloride, Carbonate, and Phosphate

Sample	Ions Present OH	Cl	CO_3	PO_4	$BaCl_2$ Used	SO_4 Present	SO_4 Found
	Mg.	*Mg.*	*Mg.*	*Mg.*	*Cc.*	*Mg.*	*Mg.*
42	2.6	2.5	1.0	..	2.10	2.50	2.45
43	2.6	2.5	1.0	..	6.1	7.50	7.35
44	2.6	2.5	1.0	0.42	2.10	2.50	2.45
45	2.6	2.5	1.0	0.42	6.1	7.50	7.35
46	2.6	2.5	1.0	0.42	18.2	22.50	22.2
47	5.2	5.0	1.0	1.25	2.50	2.50	2.50
48	5.2	5.0	1.0	1.25	6.4	7.50	7.47
49	5.2	5.0	1.0	1.25	12.6	15.00	15.10

$BaCl_2$ solution 0.025 *N*. Correction factor = 1.020.
25-cc. samples with 25 cc. of alcohol.
Blank, 0–0.6 mg. PO_4 = 0.1 cc.
0.6–1.2 mg. PO_4 = 0.3 cc.

Table V shows the results for several samples analyzed by both titration and gravimetric methods. These samples were taken from a boiler and contained the concentrations of hydroxide and carbonate shown. They also contained small amounts of calcium, silicate, and various other impurities, as well as moderate concentrations of chloride.

Conclusions

Detailed directions are given below for carrying out a determination of sulfate by direct titration using tetrahydroxyquinone as the indicator.

Reagents Needed. (1) A 0.025 *N* barium chloride solution, standardized gravimetrically. (2) A mixture of potassium chloride and tetrahydroxyquinone, prepared by grinding the disodium salt of tetrahydroxyquinone with dried potassium chloride in a 1 to 400 ratio.

Procedure. A 25-cc. sample, containing between 2 and 20 mg. of sulfate, in a 150-cc. Erlenmeyer flask, is carefully neutralized until it is just acid to phenolphthalein. The hydrochloric acid used to acidify the sample should not be stronger than 0.030 *N*, and must be added carefully from a buret. The sample should be below 30° C.

Add 25 cc. of ethyl alcohol or 25 cc. of alcohol denatured by formula 30.

Add 0.20 to 0.22 gram of the tetrahydroxyquinone–potassium chloride mixture. It is best to use a small cup to measure out the mixture. Swirl the flask until this is dissolved. This will give the solution a fairly deep yellow color.

Run in the 0.025 *N* barium chloride at a steady dropping rate with constant swirling of the flask, until a brown color begins to form. This is not the end point but indicates its approach. Add the barium chloride from here on, 2 or 3 drops at a time, with steady swirling until a red color appears; this is the end point. The red color appears throughout the body of the solution and not as spots of color. If the sample contains between 2 and 20 mg. of sulfate this titration will require less than 17 cc. of the barium chloride solution.

After deducting the 0.1-cc. blank, each cubic centimeter of the 0.025 *N* barium chloride solution is equivalent to 1.2 mg. of sulfate.

If more than 0.6 mg. of phosphate is present, the blank should be increased. For concentrations from 0.6 to 1.2 mg. of phosphate the blank should be 0.3 cc.; for concentrations from 1.2 to 1.8 mg. of phosphate the blank should be 0.6 cc.

Table V. Comparison of Results of Analysis of Samples Gravimetrically and by Titration

Sample[a]	Other Ions Present[b] OH	CO_3	Results of Analysis[c] Gravimetric SO_4	Titration SO_4
	Mg.	*Mg.*	*Mg.*	*Mg.*
1	1.1	0.16	2.60	2.48
2	2.0	0.23	9.82	9.70
3	1.7	0.22	8.75	8.72
4	2.0	0.35	10.60	10.80
5	5.2	0.16	19.40	19.20
6	6.5	0.38	23.13	23.10
7	6.7	0.38	30.13	30.90
8	3.0	0.38	15.35	15.45
9	1.5	0.20	7.35	7.25
10	1.7	0.29	8.78	8.85
11	2.0	0.13	6.45	6.40
12	2.7	0.25	7.25	7.50
13	2.3	0.22	9.08	8.98
14	2.5	0.26	9.55	9.80

[a] Samples taken from drum of an operating boiler.
[b] Chloride and small amounts of calcium, silicate, etc., present but not determined.
[c] Analyses shown, both gravimetric and titration, were carried out by S. J. Meisenberg, University of Michigan.

Analysis on aliquots diluted to 25 cc. which required less than 17 cc. of 0.025 *N* $BaCl_2$ solution. 25 cc. of alcohol added to samples.

In this direct titration the amount of various other ions which may be tolerated without causing error is 7.5 mg. of carbonate, 5 mg. of aluminum, 25 mg. of silicate, and 15 or more milligrams of magnesium. Calcium has no effect so long as the addition of the alcohol does not cause the precipitation of calcium sulfate. This precipitation must be prevented. Hydroxide and chloride are without effect. Iron above 0.1 mg. interferes and must be removed.

It is highly desirable to titrate a few samples of known sulfate concentration before using the method on unknowns. This is especially true in the present titration because the end point is somewhat different from those usually encountered and the best way to learn to recognize it is to titrate a few samples of known concentration.

The method is accurate within ±0.2 mg. of sulfate.

The use of the tetrahydroxyquinone method on solutions having a higher sulfate concentration than those indicated in the present discussion has not been investigated. It is possible that the method would be considerably more accurate in more concentrated solutions, and there are indications that the use of alcohol might be eliminated or the amount neces-

sary in the sample during the titration considerably reduced. This should offer a fertile field for further investigation.

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Distillation of Hydrocyanic Acid from Sulfuric Acid Solutions

Quantitative Determination

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Pagel and Carlson (*9*) recently published a method for the accurate determination of hydrocyanic acid in the presence of various salts (including chlorides) showing that the quantitative distillation of hydrocyanic acid from dilute sulfuric acid solution takes place within 15 minutes under specified conditions. Richards and Singer (*10*) claimed that many hours' boiling (8 to 10) is necessary to remove all the hydrocyanic acid from solutions containing appreciable amounts of chlorides, the retardation being ascribed to the formation of a complex between the chloride ion and hydrocyanic acid. Richards and Singer found that a much shorter time (less than 2 hours) suffices to remove hydrocyanic acid from solution in the absence of more than a trace of chloride ion.

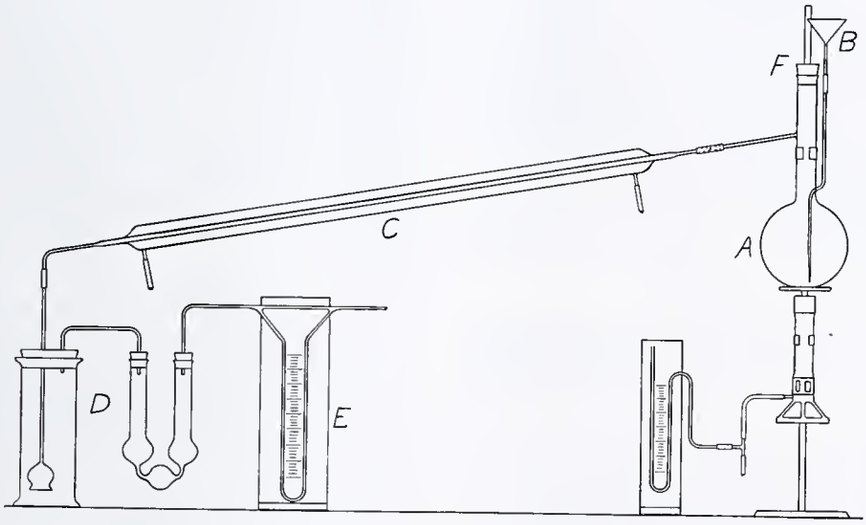

Figure 1. Diagram of Apparatus

A, 500-ml. Pyrex distilling flask with sealed-in capillary
B, long-stemmed funnel through which acid is added
C, special Pyrex condenser
D, absorption apparatus
E, flowmeter
F, tinfoil-covered rubber stopper

Method and Apparatus

When an attempt was made to determine hydrocyanic acid quantitatively by the method of Pagel and Carlson (*9*) certain difficulties were encountered which were traced to adsorption of hydrocyanic acid in the rubber stopper of the distilling flask and to the presence of ferrocyanide in the cyanides used. The optimum conditions reported in their paper were maintained. The excess sulfuric acid was calculated on the basis of the amount of cyanide used and was 0.35 *N* (*8*). Stock solutions of approximately 0.1 *N* alkali cyanides were used. The cyanide content was determined according to Liebig's method (*6*), with potassium iodide as the indicator. Titers of the stock solution were determined just before use. An enhanced Tyndall effect was obtained by using a focusing arc light (*1*).

To insure the same conditions in all experiments the flow of gas to the burner was regulated by a manometer and a flowmeter was used to regulate the flow of air through the capillary. The same pipet and buret were used throughout. Fifty milliliters of stock solution were used in all experiments. The solution in the distilling flask was heated to boiling as quickly as possible. Time of distillation was 15 minutes unless otherwise noted. Rate of distillation was 75 ml. per 15 minutes. Fifteen milliliters of 6 *N* sulfuric acid were used unless otherwise stated.

Pagel and Carlson's apparatus was modified as shown in Figure 1.

Adsorption of Hydrocyanic Acid by Stoppers

A quantitative comparison was made between determinations in which the stopper was covered with tinfoil and in which it was not, and the results are shown in Table I. The data are averages of two or more determinations. With tinfoil-covered stoppers the individual determinations agreed within 0.03 ml.

Table I. Absorption of Hydrocyanic Acid by Stoppers

Experiment	Cyanide[a] Used	Distillation	Kind of Stopper	Error
		Min.		%
1	NaCN	15	Rubber	−0.14
2	NaCN	30	Rubber	−0.12
3	NaCN	15	Rubber covered with tinfoil	−0.02
4	NaCN	15	Cork	−0.28

[a] Sodium cyanide free from ferrocyanide, prepared by distilling hydrocyanic acid into sodium hydroxide.

In two runs, when the stoppers were not protected by tinfoil, distillation was continued after the initial 15 minutes. Cuts were taken at the end of 30 and 45 minutes, and were redistilled once according to the procedure of Morris, Callaghan, and Dunlap (*7*). The distillate was tested for hydrocyanic acid by the Prussian blue method of Viehoever and Jones (*13*). All cuts gave the Prussian blue test, showing that adsorbed hydrocyanic acid was given up by the rubber stoppers.

Interference of Ferrocyanide

According to Roe (*11*) simple cyanides cannot be determined by distillation in the presence of complex cyanides. In carrying out these determinations many of the commercial brands of c. p. potassium cyanide were tested for ferrocyanide by the method of Krauch (*4*). Ferrocyanide was present in all cases tested; in but two cases was the presence admitted on the label. According to Sharwood (*12*) the presence of ferrocyanide causes high results when Liebig's method is used. This was confirmed by adding potassium ferrocyanide to sodium cyanide and titrating in the usual manner.

Ferrocyanide gave high results in all the cases where it was present.

Feld (*2*) reports that the simple cyanides may be determined in the presence of complex cyanides by distilling the mixture with magnesium chloride. The magnesium chloride yields sufficient hydrochloric acid to displace the hydrocyanic acid from the simple cyanides, but not from the complex cyanides. Tartaric acid is frequently recommended in cyanide distillations, especially in forensic examinations. The results obtained with these various reagents upon different cyanides are reported in Table II.

Table II. Distillation with Various Reagents

Experiment	Cyanide Used	Reagent Used	Error
			%
1	KCN[a]	H_2SO_4	+0.69
2	KCN[b]	H_2SO_4	+0.72
3	NaCN[c]	H_2SO_4	−0.02
4	NaCN[c]	$MgCl_2$[d]	−0.08
5	NaCN[c]	$MgCl_2$[e]	−0.04
6	KCN[a]	$MgCl_2$[e]	−0.22
7	NaCN[c]	$H_2C_4H_4O_6$[f]	−0.07
8	NaCN[c]	H_2SO_4[g]	−0.04

[a] Well-known brand of c. p. KCN.
[b] Second well-known brand of c. p. KCN.
[c] Ferrocyanide-free sodium cyanide.
[d] 60 ml. of 3 *N* $MgCl_2$.
[e] 15 ml. of 3 *N* $MgCl_2$.
[f] 15 ml. of 6 *N* tartaric acid.
[g] 1 to 5 grams of NaCl were added during these runs.

The data are averages of two or more determinations. Tinfoil-covered stoppers were used throughout.

Hydrolysis of Hydrocyanic Acid

It will be noted that the error in all the determinations on ferrocyanide-free sodium cyanide is a negative one. Part of this loss is due to hydrolysis of hydrocyanic acid to ammonium formate. In a few cases the amount of hydrolysis during distillation was determined by a modification of the method of Gales and Pensa (*3*). After distilling off the hydrocyanic acid for a stated time (15 minutes) sodium hydroxide solution was added to the distilling flask and the ammonia was distilled off and determined in the distillate by nesslerization. A blank determination was made on the reagents and this value subtracted from the total amount of ammonia found. It is impossible, of course, to determine the amount of ammonia present in the cyanide solution directly by nesslerization; so a freshly prepared solution of sodium cyanide was used. In one case the amount of hydrolysis under the usual conditions was determined. The average error of four determinations was −0.06 per cent. An average of 0.04 mg. of nitrogen was found in the distillate after the addition of the sodium hydroxide. Making correction for this hydrolysis, the final error of the determination was +0.008 per cent. In another series (error −0.02 per cent) after correction for hydrolysis the final error was +0.04 per cent.

Since Krieble and Peiker (*5*) have shown that the rate of hydrolysis is dependent upon the acid concentration, it is advantageous to keep the concentration of the acid low.

Recommended Procedure

In order to avoid loss of hydrocyanic acid by adsorption, rubber stoppers should be covered with tinfoil, or ground-glass joints should be used. By modifying the condenser as shown in Figure 1 a good joint can be made with heavy rubber tubing, which exposes very little rubber to the distillate. In order to avoid excessive hydrolysis, the concentration of acid should be kept low; the excess acid should be kept within 0.35 *N*. Either sulfuric or tartaric acid may be used to liberate the hydrocyanic acid. Fifteen minutes' distillation, when the total volume is 250 ml., is sufficient to remove all the hydrocyanic acid from solution when the rate of distillation is 300 ml. per hour. A slight vacuum should be maintained on the distilling flask at all times.

Summary

No evidence was found that the distillation of hydrocyanic acid from sulfuric acid solutions was retarded by the presence of the chloride ion; this supports the findings of Pagel and Carlson rather than those of Richards and Singer. It was found that the removal of hydrocyanic acid was rapid and complete when stoppers were protected with tinfoil. Unprotected rubber stoppers and corks were found to adsorb hydrocyanic acid and very slowly give it up again. Ferrocyanide has been found to be a common impurity in commercial c. p. alkali cyanides; and when such cyanides are determined by distillation they give high results, owing to the decomposition of ferrocyanide. The method of Feld permits the determination of simple cyanides in the presence of complex cyanides, but the results are rather low. With ferrocyanide-free cyanides and using protected rubber stoppers, the method of Pagel and Carlson is accurate within 0.05 per cent. The rate of hydrolysis of hydrocyanic acid is a function of acid concentration.

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A Convenient Weighing Buret

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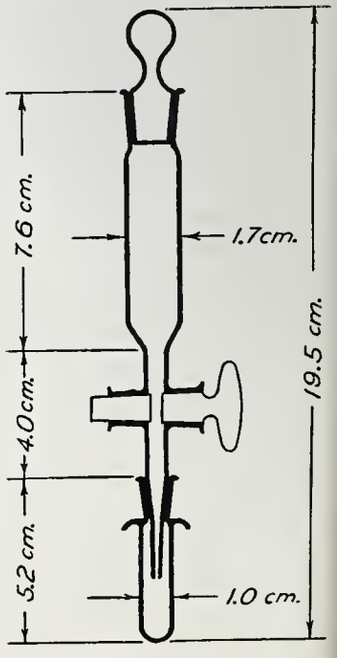
The accompanying illustration represents the cross section of a weighing buret that has been found to be of good design and convenient to use. Such a buret, having a graduated barrel, may be made from an old buret.



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Technic in Chemical Analyses of Casein

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In a former paper (*11*) a comparison of approved methods of analyzing casein showed considerable variation in results and indicated the necessity of further study with the hope of evolving standard methods of analysis. Browne (*5*), Shaw (*9*), and Sutermeister (*10*), who have reported on the physical and chemical analysis of casein, state that further study is necessary because of discrepancies occurring in results of various analysts. Zoller (*12*) in 1920 reported on the borax solubility test for commercial casein and suggested a modified test to differentiate between caseins made at high and low temperatures.

In the present paper studies have been made on methods of determining moisture, ash, nitrogen, fat, free acidity, total acidity, pH values, solubility, and conductivity. The samples used in this work were selected at random from sixty-five commercial lots of casein made by the natural-sour method.

Moisture

In Tables I and II are given summaries of the effect of different temperatures and amounts of vacuum used in drying samples from various commercial plants in Idaho.

An attempt was first made to obtain constant weights on samples dried at 102° C. Samples were weighed at periods of 5, 8, 24, and 30 hours and steadily increasing percentages of loss were obtained. A temperature of 90° C. was then tried in an attempt to find a lower temperature at which excessive losses did not occur. Losses continued to take place, although in lesser amounts than at 102° C., and were attributed largely to caramelization, because the samples gradually turned darker as they were heated longer. Whether the excess loss is due entirely or partially to caramelization or to changes in molecular structure was not determined. The temperature was then lowered to 80° C. and in order to hasten loss of moisture the samples were placed in a vacuum of 11 inches. No caramelization took place and constant weights were obtained in 24 hours. This method of 80° C. with 11 inches of vacuum was used as standard in determining moistures.

It was felt that this method required too much time to be practical for use in commercial laboratories, and that a shorter period of time with higher temperature, or with higher temperature and increased vacuum, might be used. Table II gives results of moistures determined at 100° C., 90° C. with 11 inches of vacuum, 100° C. with 22 inches of vacuum, and 135° C. with 22 inches of vacuum. Determinations were made at intervals of 0.5, 1, 2, 3, 4, and 5 hours.

Variations in length of time required to obtain moistures of different samples made it practically impossible to set a definite time limit which would be applicable in all cases. Closely agreeing results can be obtained at higher temperatures and in shorter periods of time, but the uncertainty as to whether these results are higher or lower than the true moistures leads to the conclusion that such methods should not be used except in cases where only approximate determinations are desired.

Ash

The determination of ash was very difficult because of spattering. Various methods were used in an attempt to control this problem.

1. Samples were charred slowly on a hot plate for 5 hours, then placed in a cold muffle and gradually heated to 650° C., which usually required from 2.5 to 3 hours. The samples were held at this temperature from 5 to 6 hours or until a white ash was secured.
2. Samples were charred on a hot plate 5 hours, 5 cc. of concentrated nitric acid were added, and heated in the muffle as above.
3. Samples were charred on a hot plate 5 hours, varying amounts of calcium acetate were added (5 and 3 cc. of a 10 per cent solution), then heated in the muffle as above. Blank determinations gave the amount of calcium oxide left on burning.
4. Same as (3) except that calcium acetate was added before charring.
5. Five and 3 cc. of calcium acetate were added, and samples were placed directly in the cold muffle without charring and heated as in (1).

Two-gram samples of casein were used in all ash determinations. The results are given in Table III. The best checks and highest ash content were obtained when 5 cc. of calcium acetate were added to the sample and placed in the cold muffle without previous charring. It is necessary to bring all the casein in contact with the calcium acetate solu-

Table I. Comparison of Methods of Determining Moisture Content of Casein

Sample	102° C. 5 hrs.	102° C. 8 hrs.	102° C. 24 hrs.	102° C. 30 hrs.	90° C. 5 hrs.	90° C. 8 hrs.	90° C. 24 hrs.	90° C. 30 hrs.	80° C. + 11-Inch Vacuum 5 hrs.	80° C. + 11-Inch Vacuum 8 hrs.	80° C. + 11-Inch Vacuum 24 hrs.	80° C. + 11-Inch Vacuum 30 hrs.
	%	%	%	%	%	%	%	%	%	%	%	%
1	5.25	5.18	5.26	5.57	4.78	4.79	5.25	5.65	4.13	4.28	4.39	4.38
2	5.42	5.54	5.49	5.89	4.61	4.68	5.27	5.46	4.17	4.27	4.84	4.59
3	5.35	5.48	5.50	5.58	4.59	4.68	5.25	5.17	3.95	3.99	4.48	4.34
4	7.60	7.72	7.78	7.82	7.08	7.02	7.55	7.73	6.46	6.68	7.00	7.03
5	5.46	5.47	5.48	5.64	4.97	4.98	5.30	5.34	4.04	4.63	4.70	4.67
6	5.52	5.50	5.68	5.87	5.43	5.44	5.54	5.54	4.75	4.95	4.99	5.05
7	4.50	5.29	5.34	5.55	4.57	4.76	4.83	4.87	3.89	4.34	4.36	4.29
8	4.74	5.01	5.20	5.18	4.62	4.98	5.10	5.09	3.31	3.78	3.86	4.11

Table II. Comparison of Methods of Determining Moisture Content of Casein

Sample	100° C. 0.5 hr.	100° C. 1 hr.	100° C. 2 hrs.	100° C. 3 hrs.	100° C. 4 hrs.	100° C. 5 hrs.	90° C. with 11-Inch Vacuum 0.5 hr.	90° C. 1 hr.	90° C. 2 hrs.	90° C. 3 hrs.	90° C. 4 hrs.	90° C. 5 hrs.	100° C. with 22-Inch Vacuum 1 hr.	100° C. 2 hrs.	100° C. 3 hrs.	100° C. 4 hrs.	100° C. 5 hrs.	135° C. with 22-Inch Vacuum 0.5 hr.	135° C. 1 hr.	135° C. 2 hrs.	135° C. 3 hrs.	135° C. 4 hrs.	135° C. 5 hrs.
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	3.46	4.30	4.33	4.82	5.03	5.03	2.83	3.55	4.64	4.85	4.95	5.10	5.03	5.41	5.47	5.50	5.51	5.40	5.79	6.05	6.25	6.36	6.61
2	3.67	5.12	5.45	6.01	6.28	6.34	2.92	3.69	4.72	5.00	5.18	5.34	5.21	5.58	5.88	5.96	5.96	5.54	6.11	6.50	6.74	6.88	7.03
3	3.48	4.36	4.93	5.12	5.33	5.48	3.05	3.93	4.80	5.01	5.16	5.31	5.36	5.60	5.76	5.80	5.82	5.80	6.21	6.50	6.73	6.90	7.02
4	3.95	5.27	5.38	6.03	6.16	6.20	3.52	4.71	5.49	5.83	5.82	5.98	6.05	6.34	6.40	6.46	6.47	6.44	6.64	6.98	7.13	7.16	7.13
5	3.18	4.34	5.21	5.33	5.54	5.69	3.52	4.00	5.05	5.33	5.41	5.62	5.54	5.93	5.99	6.03	6.03	5.60	6.08	6.41	6.51	6.55	6.66
6	3.56	4.34	5.20	5.57	5.72	5.81	3.35	3.38	5.17	5.37	5.47	5.59	5.48	5.92	6.01	6.05	6.05	5.41	6.07	6.39	6.60	6.64	6.73
7	2.65	3.84	4.80	5.05	5.35	5.47	2.92	3.67	4.65	4.98	5.07	5.25	4.96	5.52	5.61	5.65	5.69	5.40	5.95	6.22	6.37	6.41	6.58
8	2.56	3.49	4.37	4.87	5.15	5.22	2.56	3.25	4.32	4.57	4.76	4.93	4.42	5.05	5.26	5.33	5.33	4.98	5.76	5.98	6.12	6.18	6.33

tion and allow it to stand for about 20 minutes before placing in the muffle. This permits the casein to become thoroughly moistened and apparently aids in the prevention of spattering. Three cubic centimeters of calcium acetate solution did not seem to be a sufficient amount to moisten the entire sample and prevent spattering.

When the sample was charred on the hot plate without the addition of calcium acetate, some spattering occurred. When calcium acetate was added before charring, the sample apparently dried out on the hot plate and there was some spattering in the muffle. When nitric acid was added, spattering always took place, regardless of whether it was added before or after charring or placed directly in the muffle. Spattering can never be prevented when the temperature in the muffle is raised too fast. Best results were obtained when 2.5 to 3 hours were allowed to raise the temperature to 650° C.

Table III. Comparison of Methods of Determining Ash Content of Casein

(5.5 hours in muffle at 650° C.)

Sample	Charred	Charred 5 cc. HNO_3 Added	Calcium Acetate Used: Added after charring 3 cc.	Added after charring 5 cc.	Added before charring 3 cc.	Added before charring 5 cc.	No charring 3 cc.	No charring 5 cc.
	%	%	%	%	%	%	%	%
1	2.75	3.25	3.31	3.29	3.40	3.31	3.29	3.79
2	3.20	3.21	3.09	3.20	3.37	3.11	3.00	3.37
3	2.71	4.71	3.16	3.39	3.50	3.73	2.71	4.17
4	3.00	3.79	3.40	3.51	3.26	3.32	2.94	3.94
5	2.73	2.66	3.11	2.98	3.10	3.37	3.36	3.45
6	3.52	3.61	3.32	3.44	3.31	3.42	2.88	3.47
7	1.92	3.38	3.05	2.97	3.36	3.44	2.97	3.50
8	2.99	2.67	3.19	3.19	3.38	3.18	1.93	3.55

Nitrogen

In Table IV are presented the results on total nitrogen determined by the Gunning method and Kjeldahl mercury method (*2*), with the exception that the samples were digested longer than the 2 hours suggested. The samples were digested over ordinary gas burners using gasoline gas, on which a pyrometer registered a heat of approximately 850° C. It is possible that higher heats might have brought about complete digestion in a shorter period of time. Sutermeister (*10*) states there is present in casein from 1.2 to 3.43 per cent of humin nitrogen largely derived from tryptophane, which is rather difficultly hydrolyzed even in strong acids. It is therefore questionable whether a 2-hour digestion will render all the nitrogen available. In the authors' experiments at least 4 hours with the Gunning method and 6 hours with the Kjeldahl mercury method were required to bring about complete digestion. The Kjeldahl mercury method seemed somewhat slower than the Gunning method in bringing about complete digestion and the final results even after 8 hours were slightly lower, although the difference was so small as to be negligible.

Table IV. Total Nitrogen Calculated on Moisture-Free Basis

Sample	Gunning Method 1 hr.	Gunning Method 4 hrs.	Gunning Method 6 hrs.	Gunning Method 8 hrs.	Kjeldahl Mercury Method 1 hr.	Kjeldahl Mercury Method 4 hrs.	Kjeldahl Mercury Method 6 hrs.	Kjeldahl Mercury Method 8 hrs.
	%	%	%	%	%	%	%	%
1	13.36	14.16	14.33	14.25	13.34	14.04	14.24	14.21
2	13.03	14.13	14.21	14.21	13.48	13.98	14.15	14.15
3	13.14	14.10	14.14	14.14	13.18	13.91	14.07	14.09
4	13.26	14.27	14.34	14.31	13.47	14.04	14.26	14.29
5	13.16	14.37	14.41	14.40	13.22	14.06	14.21	14.31
6	13.72	14.34	14.34	14.34	13.60	14.02	14.23	14.25
7	13.36	14.13	14.15	14.16	13.20	13.80	13.96	13.96
8	13.32	14.19	14.19	14.20	12.95	13.80	13.92	13.94

Table V presents data showing the calculation of nitrogen on the moisture-free basis and the moisture-, fat-, and ash-free basis as recommended in the usual method of procedure.

According to the United States Government specifications for water-resistant glues for use in airplanes as given by Bogue (*3*), casein must contain not less than 14.25 per cent nitrogen, calculated on the moisture-, fat-, and ash-free basis. The American Medical Association (*1*) states that "calcium casein should contain not less than 1 per cent calcium, 0.6 per cent phosphorus, and 14 per cent nitrogen on the moisture-free basis."

Table V. Total Nitrogen by Gunning Method

(4 hours' digestion)

Sample	1	2	3	4	5	6	7	8	Pure Casein (Hammarsten)
	%	%	%	%	%	%	%	%	%
Moisture-free basis	14.16	14.13	14.10	14.27	14.37	14.34	14.13	14.19	15.08
Moisture-, fat-, and ash-free basis	14.80	14.69	14.75	14.87	15.02	14.95	14.78	14.74	15.53

A number of impurities are present in casein, such as mineral salts, fat, albumen, lactose, and acids. Other research workers have felt that it is possible to estimate to a certain extent the undetermined impurities in casein by calculating nitrogen on the moisture-, ash-, and fat-free basis. However, since the determination of nitrogen in casein is meant to show not merely the undetermined impurities but rather the total amount of impurities present in the sample, the authors feel that the determination should be made on the moisture-free basis only.

Comparative determinations were made as to length of time required for digestion on gas and electric burners. Further work was also done, using selenium oxychloride as a catalyst, recently recommended by Lauro (*6*), Osborn and Krasnitz (*8*), Messman (*7*), and others. Various combinations of catalysts were also used, as shown in Table VI.

Table VI. Total Nitrogen Calculated on Moisture-Free Basis

(Sample F16)

Electric Burners: Hrs.	Na_2SO_4 + $CuSO_4$	Na_2SO_4 + $CuSO_4$ + $SeOCl_2$	Na_2SO_4 + Hg + $SeOCl_2$	Na_2SO_4 + $CuSO_4$ + Hg + $SeOCl_2$	Gas Burners: Hrs.	Na_2SO_4 + $CuSO_4$	Na_2SO_4 + $CuSO_4$ + $SeOCl_2$	Na_2SO_4 + Hg + $SeOCl_2$	Na_2SO_4 + $CuSO_4$ + Hg + $SeOCl_2$
	%	%	%	%		%	%	%	%
0.5	...	14.16	14.20	14.23	1	...	14.16	14.37	14.37
1	14.13	14.37	14.25	14.44	2	14.30	14.33	14.41	14.35
1.5	14.22	14.40	14.45	14.37	3	...	14.35	14.43	14.35
2	14.37	14.37	14.41	14.25	4	14.38	14.37	14.46	14.37
4	14.38	14.40	...	...	6	14.39	14.39	...	...

With the higher heat of the electric burners a considerable saving in length of time was experienced, digestion being complete in 2 hours. With selenium oxychloride in addition to copper sulfate, mercury, or copper sulfate and mercury in combination, the time of digestion was shortened to 1 hour on the electric burners and 2 hours on the gas burners. With the three catalysts in combination, 1 hour apparently was sufficient to obtain all the nitrogen on the gas burners. When the samples were digested longer than 2 hours on the electric burners a loss occurred in the nitrogen due to evaporation of the sulfuric acid and increase of concentration of salts in the solution. These losses were prevented by additions of sulfuric acid as required. No losses of nitrogen occurred with the gas burners, regardless of the length of time of digestion.

Fats

Table VII gives the results of fat determinations by various methods. The ether extraction was made in the regular way (*2*), using a 2-gram sample of casein and extracting for 48 hours. The sample was ground to pass a 20-mesh sieve, giving various degrees of fineness from 100 mesh to 20 mesh. A 1-gram sample was used in the Roese-Gottlieb method: 10 cc. of water, 2 cc. of concentrated

ammonia, and 10 cc. of 95 per cent alcohol were added, shaken until completely dissolved, and the fat extracted in the usual way with ether and petroleum ether. Results by this method were much higher than by other methods because of the fact that a white colloid-like substance passed through the filter paper along with the dissolved fat. This material precipitated out in the flask on partial evaporation of the ether. Attempts were made to filter it out at this stage, but the final results, while lower, were so inaccurate, owing to the small amount of fat and the uncertainty as to whether all the colloidal material had been filtered out, that the method was finally abandoned.

Table VII. Influence of Method of Analysis on Per Cent Fat

Sample	Ether Extraction	Roese-Gottlieb	Babcock
1	0.37	1.16	0.36
2	0.27	0.97	0.36
3	0.22	0.68	0.27
4	0.13	1.03	0.14
5	0.34	1.64	0.28
6	0.29	1.79	0.32
7	0.32	1.89	0.32
8	0.18	1.52	0.16

Table VIII. Effect of Size of Casein Particles on Fat Extraction

(Adams ether extraction 48 hours)

Sample	100 Mesh	65 Mesh	40 Mesh	20 Mesh
	%	%	%	%
11	0.31	0.28	0.14	0.15
12	0.26	0.26	0.23	0.16
13	0.28	0.22	0.12	0.12
14	0.50	0.29	0.21	0.20
15	0.37	0.14	0.05	0.05

The Babcock method used, given by Sutermeister (*10*), approximates very closely the official ether extraction method, and is probably the best practical method to use in commercial plants. Attempts were made to dissolve the casein in various other solvents than those given by Sutermeister, such as sodium borate, sodium phosphate, and ammonium and sodium hydroxides. These solvents dissolved the casein very rapidly, but when sulfuric acid was added the reaction was so violent that it was almost impossible to prevent some loss of the sample from the bottle. The best results were obtained by the use of 1 gram of casein, 10 cc. of water, 4 cc. of butyl alcohol, and 2 cc. of concentrated ammonium hydroxide. The casein dissolved readily and did not cause very violent reaction when 15 cc. of concentrated sulfuric acid were added.

The Mojonnier method was also tried, but the same difficulties were found as in the Roese-Gottlieb method.

In Table VIII is shown the effect of the size of casein particles upon fat solubility by the ether extraction method. The results are self-evident. Apparently some fat is held within the larger particles of casein so that it cannot be extracted. No attempt was made to grind the casein finer than 100 mesh, and it is possible that a small amount of fat remained in the casein, but it was felt that this degree of fineness is sufficient to obtain practically all the fat. In fat determination on casein, therefore, the authors believe that the ether extraction method is the most accurate of any tried, providing the sample is ground to 100 mesh and extracted for at least 48 hours.

Comparison of Free Acidity, Total Acidity, pH Value, Conductivity, Solubility, and Ash Content

Table IX gives the results on free acidity, total acidity, pH value, conductivity, and ash on eight commercial samples of casein and a pure casein (Merck, purified according to Hammarsten).

Free acidity was determined by adding 100 cc. of water to 10 grams of casein, allowing it to stand for five hours, filtering and titrating 50 cc. of the filtrate with 0.1 *N* sodium hydroxide. Total acidity was obtained by dissolving 1 gram of casein in 25 cc. of 0.1 *N* sodium hydroxide, adding 50 cc. of water, and titrating back with 0.1 *N* sulfuric acid, using phenolphthalein as an indicator. pH values were determined by both the hydrogen electrode and quinhydrone methods, using a 5 per cent suspension of casein. In determining conductivity, a 5 per cent suspension of casein was used in specially prepared conductivity water and allowed to stand for 17 hours, or overnight, before running.

Ash was determined by the calcium acetate method discussed previously. Solubility was determined in minutes required completely to dissolve a given amount of casein in 300 cc. of a 2.5 per cent solution of sodium borate at 65° C.

In the determination of pH values the stirring hydrogen-electrode method developed by Bollen (*4*) was used. Comparisons were made with the quinhydrone method in order to determine whether this simpler method could be used. No practical differences were obtained and it is felt that for all practical purposes the quinhydrone method may be used for determination of pH values on casein.

In Table X is given a comparison of the effects of time, strength of solution, and size of particles on pH values. The casein was allowed to stand for at least 1 hour in solution in order that it might become thoroughly saturated. Since no differences were obtained regardless of fineness of particles, length of time in solution after 1 hour, or amounts of casein in solution, it was decided to use the 5 per cent suspension because of the greater ease of handling.

Table X. Effect of Strength of Solution and Size of Casein Particles on pH Value

	Effect of Amount of Casein on pH Value						Effect of Size of Particles of Casein on pH Value			
	5 %		10 %		20 %	50 %	20 mesh	40 mesh	65 mesh	100 mesh
Hours										
1	3.80	3.82	3.83	3.88	..	..	3.95	3.90	3.92	3.92
18	3.80	3.80	3.85	3.85	3.85	3.93	3.88	3.88	3.88	3.92

In Table XI is shown the effect of these same factors upon conductivity. Apparently at least 17 hours or overnight standing in solution is necessary to reach a constant. Fineness of particles also has considerable effect, the salts seeming to go into solution much more rapidly when the casein is ground to smaller mesh. However, there is no difference in conductivity if the sample is allowed to stand overnight. Slightly higher results were obtained when a 5 per cent suspension was used, probably because of a more complete solution of the salts present. The 5 per cent suspension was decided upon as the more convenient to use.

Table IX. Comparison of Free Acidity, Total Acidity, pH Value, Conductivity, and Ash of Nine Samples of Casein

Sample	Free Acidity	Total Acidity	Hydrogen Electrode pH	Quinhydrone pH	Conductivity	Resistance	Solubility 10 Grams Casein	Ash Content
	Cc.	*Cc.*				*Ohms*	*Min.*	%
1	12.70	14.72	3.90	3.99	1.41×10^{-3}	709.0	8.5	3.79
2	12.85	14.75	3.90	3.91	1.40×10^{-3}	714.0	6.0	3.37
3	12.10	14.62	3.97	4.04	1.62×10^{-3}	617.0	7.5	4.06
4	11.65	14.50	3.91	4.12	1.40×10^{-3}	714.0	6.0	3.69
5	7.15	14.10	4.21	4.21	1.01×10^{-3}	990.0	5.5	3.63
6	7.85	13.90	4.27	4.28	1.21×10^{-3}	825.0	5.5	3.56
7	9.55	13.60	4.11	4.10	1.19×10^{-3}	840.0	6.5	3.85
8	10.95	14.01	3.81	3.85	0.975×10^{-3}	1025.0	6.0	3.47
Pure casein (Hammarsten)	1.60	9.75	5.64	5.64	0.148×10^{-3}	6754.0	1.0	2.44

Table XI. Effect of Strength of Solution and Size of Casein Particles on Conductivity

Casein in Solution	Conductivity				
	Immediately	4 hours	6 hours	17 hours	45 hours
%					
5	0.72×10^{-3}	1.20×10^{-3}	1.54×10^{-3}	1.43×10^{-3}	1.40×10^{-3}
10	1.88×10^{-3}	2.55×10^{-3}	2.77×10^{-3}	2.68×10^{-3}	2.67×10^{-3}
20	2.31×10^{-3}	4.10×10^{-3}	4.51×10^{-3}	4.97×10^{-3}	4.95×10^{-3}
Particle Size	10 Per Cent Solution				
20 mesh	1.88×10^{-3}	.....	.....	2.73×10^{-3}	.....
40 mesh	2.35×10^{-3}	.....	.....	2.73×10^{-3}	.....
65 mesh	2.53×10^{-3}	.....	.....	2.75×10^{-3}	.....
100 mesh	2.62×10^{-3}	.....	.....	2.76×10^{-3}	.....

Considerable difficulty was experienced in an attempt to arrive at a solubility factor for the various caseins. The regular procedure of using 50 grams of casein in 300 cc. of 2.5 per cent sodium borate solution heated to 65° C. was followed. It was found impossible to determine the end point accurately, because of the milky whiteness of the solution, which obscured the last particles of casein to such an extent that one could not see whether they were in solution or not. The method was modified after various trials with different indicators by the addition of 1 cc. of a 1 per cent solution of corallin in alcohol. This gave a red color to the casein solution which permitted easy visibility of the particles not in solution. It was found by this method that casein ground to pass a 20-mesh sieve dissolved rather readily in fairly definite lengths of time, but that a few larger lumps were always left which would not dissolve even in an hour's time. The method was then modified, using the same strength of sodium borate solution and the same temperature, but dissolving only 10 grams of casein. Complete solution was obtained by this method.

The results are given in Table IX. Since the value of the borax test lies in its ability to give direct evidence as to the value of a casein for glue-making, paper-sizing, etc., further work must be done upon this phase of the problem before any definite conclusions may be drawn.

From the results given in Table IX, it seems evident that some relation exists between acidity, pH values, conductivity, and solubility. Where acidity is low and conductivity shows a high resistance there is always a tendency toward a low ash content and a rapid solubility. When the commercial samples are compared with the analyses of pure casein (purified according to Hammarsten), this fact becomes self-evident. Pure casein gives a much lower free acidity and a considerably higher resistance in ohms, while the ash content is lower and the solubility much more rapid. The pH value also indicates that there is much less acidity in the sample of pure casein than in the commercial caseins.

The method of treatment of the commercial sample in its preparation will obviously have a considerable influence on all methods of analysis proposed, but in the authors' estimation the sensitivity of conductivity to variable factors gives it an importance above all other methods in determining the impurities present in the sample. pH values also aid in determining the acidity of the sample and should be studied along with the free acidity and total acidity determinations.

Methods of analysis for moisture, ash, nitrogen, fat, pH value, and conductivity as recommended in this paper have been used by five research workers in analyzing approximately three hundred samples of casein. Extremely satisfactory results have been obtained.

Summary

In order to determine moisture accurately it is necessary to use temperatures which will not cause caramelization of the sample. The best results were obtained when the samples were dried in vacuum at 80° C. for 24 hours, a sufficient time to produce constant weight.

Regardless of care in manipulation, it was found impossible to burn the samples for ash by ordinary methods and obtain accurate results. Spattering always occurred when nitric acid was added or when calcium acetate was used in too small amounts. Charring the sample previous to burning in the muffle aided only partially. The only method that gave accurate checks was the use of 5 cc. of calcium acetate solution, allowing it to stand in contact with the casein for 20 minutes, then placing it in the cold muffle and gradually bringing to a temperature of 650° C. The burning was continued at this temperature until a white ash was obtained.

In total nitrogen determinations it was found necessary to digest the sample at least 4 hours by the Gunning method and 6 hours by the Kjeldahl mercury method on gas burners before all the nitrogen was obtained. Electric burners shortened the length of time of digestion to 2 hours. When selenium oxychloride was added to the copper sulfate, mercury, or copper sulfate and mercury in combination, the length of time of digestion was shortened to 1 hour on the electric burners and 2 hours on the gas burners.

The modified Babcock test for fat gave results agreeing very closely with the official ether extraction method. The official method gave the best results, if the sample was ground to at least 100 mesh and extracted for 48 hours.

The quinhydrone method of determining pH values of casein can be used satisfactorily.

The determination of conductivity is proposed as an additional aid in evaluating caseins. Its extreme sensitivity to variable factors in the preparation of caseins makes its determination of value.

Further studies are being carried out on the solubility factor. Present methods are rather unsatisfactory when accurate analysis is desired.

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Scientists of the Bureau of Standards have developed a modified type of ink which, it is believed, will have no deteriorating effect on paper. Experts found, by inking papers and subjecting them to accelerated aging by the application of heat, that the ordinary type of writing ink caused rapid embrittlement of the papers. In some cases folding endurance was decreased by as much as 50 per cent. After many experiments, the ink found satisfactory in this connection is alkaline, ammonia replacing the acid of the usual type of ink. There was practically no embrittlement of papers inked with the newly developed preparation when they were subjected to the heat test.

Determination of Sulfuric Anhydride in Sulfonated Oils and Other Products

New Direct Gravimetric Method

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IN THE analysis of sulfonated (sulfated) oils for organically combined sulfuric anhydride by the present direct method (*1*) or the sulfuric acid titration method, the sample is boiled with sulfuric acid and the increase in acidity, which corresponds to the organically combined sulfur, is determined volumetrically in the presence of methyl orange indicator. The method is rapid and reliable, and has replaced to a considerable extent, in this country as well as abroad, the old gravimetric method consisting of two barium sulfate determinations. The method, however, fails in the presence of titratable salts, such as sodium acetate, that do not give a sharp end point with indicators. Moreover, the titration method as well as the old gravimetric method is not applicable to oils of the true sulfonic type which are not hydrolyzed by acids.

In connection with an investigation of sulfonated oils by a committee, of which the writer is chairman, appointed by the American Association of Textile Chemists and Colorists, a new direct gravimetric method has been developed by the writer—the ash-gravimetric method—which seems applicable to all types of sulfonated oils, including those containing troublesome titratable salts. The ash-gravimetric method consists essentially in isolating the sulfonated compound free from inorganic salts and determining the ash of the purified product. The method is direct in the sense that it requires only one determination and the inorganic sulfate present in the oil need not be determined separately.

Preliminary tests have indicated that the new method will determine the combined sulfur not only in sulfonated oils of the usual kind—i. e. ester type—but in special sulfonated products, such as sulfonated mineral oils, sulfonated saponifiable oils of the true sulfonic type, sulfonated aromatic hydrocarbons, and sulfonated fatty alcohols, esters, and other compounds which have recently appeared on the market (Nekal, Gardinol, Igepon etc.) as substitutes for soap and wetting-out agents. The only requirement in the successful application of the method is that the product may be completely extracted by solvents over a saturated solution of sodium chloride or sulfate.

It was found that the ash of the pure sulfonated product consists of sodium sulfate and represents just half of the organically combined sulfuric anhydride. The reaction during ignition is as follows, where R stands for the organic radical:

$$2R\text{-}SO_4Na \longrightarrow Na_2SO_4 + SO_3 + \text{etc.}$$

or

$$2R\text{-}SO_3Na \longrightarrow Na_2SO_4 + SO_3 + \text{etc.}$$

In the calculation it is assumed that the ash consists of sodium sulfate rather than potassium or other metal sulfate. This assumption applies to nearly all commercial oils, since the sulfonic (or sulfate) group is almost completely neutralized during the washing, which is usually done with a solution of either sodium chloride or sulfate.

PROCEDURE

The procedure is varied somewhat, depending upon whether or not the product contains ammonia, and whether or not when dissolved in ether it forms emulsions with saturated salt solutions.

A. REGULAR PROCEDURE. Weigh 10 grams of the sample into a 250-cc. pear-shaped separatory funnel containing 50 cc. of 25 per cent sodium chloride solution. Add 5 drops of a 0.1 per cent solution of methyl orange and 75 to 100 cc. of ether, and acidify with approximately normal sulfuric acid until the lower layer is distinctly pink (about 0.2 cc. excess). Add solid sodium chloride equal to one-third of the acid added, shake vigorously until the salt is practically dissolved, and allow the layers to separate.

Draw off the lower layer into another separatory funnel and wash the ether layer with 25 cc. of the salt solution. Combine the salt layers and extract twice with 20-cc. portions of ether. Combine the ether layers and, after carefully removing any water that may settle, shake well for 3 to 5 minutes with 10 cc. of 25 per cent sodium sulfate solution, at 50° C. Separate the lower layer as completely as possible, warming it in warm water or with steam to keep the salt from crystallizing. After the water layer is removed, however, crystallization of any salt that may be dissolved in the ether layer should be induced by cooling to about 15° C. and, if necessary, by scratching the wall of the funnel with a glass rod.

Filter into a dry 250-cc. beaker, washing the funnel and crystals, if any, with three 10-cc. portions of ether or until all the fatty matter has been transferred. Cool the filtered ether solution in ice water for 15 minutes, warm to 25° to 30° C., filter again into a dry 300-cc. flask, and wash the beaker and filter paper with three 10-cc. portions of chilled ether. The filtered solution when again chilled to 0° C. and warmed to 25° to 30° C. should remain perfectly clear. A flocculent precipitate during chilling that does not clear upon warming indicates insufficient solvent to keep the fat in solution at that temperature, in which case more solvent should be added.

Distill off the ether until the volume has been reduced to about 20 cc. and transfer to a tared 50-cc. crucible (high form), which is allowed to float in a 100-cc. beaker filled with warm water. Rinse the flask with two 10-cc. and two 5-cc. portions of ether, respectively, or until all the oil has been transferred to the crucible, each addition being made only after the ether of the previous portion has practically evaporated. Care should be taken during the evaporation to prevent loss of oil by creeping; this may be avoided and the evaporation hastened by constant stirring with a glass rod, which is ultimately wiped clean with ashless filter paper that is added to the crucible. After the ether is evaporated, burn the oil gently and ignite to constant weight. To complete the oxidation of any remaining carbon or traces of sulfide that may be formed, moisten the ash with a few drops of 30 per cent hydrogen peroxide and again carefully ignite to constant weight.

B. PROCEDURE IN PRESENCE OF AMMONIA. Dissolve 10 grams of the sample in 80 cc. of water in a 300-cc. beaker, add 10 cc. of 0.5 *N* sodium hydroxide, and boil the solution gently until wet litmus paper no longer indicates ammonia. Cool and transfer into a 300-cc. pear-shaped separatory funnel and add about 33 grams of solid sodium chloride, or enough to make finally a 25 per cent salt solution. Add 5 drops of a 0.1 per cent solution of methyl orange and proceed with the neutralization and extraction as directed in A.

C. PROCEDURE IN CASE EMULSIONS FORM. Dissolve the sample in 50 cc. of water and transfer carefully to a separatory funnel. Add 100 cc. of ether and enough solid sodium chloride to saturate the water layer and leave some solid salt in excess. Shake well, add methyl orange indicator, and acidify as directed under regular procedure. If emulsions form, add 2 cc. of alcohol at a time until the emulsion breaks, mixing gently but not shaking after each addition of the alcohol. Proceed then following procedure A, except that whenever emulsions are formed, break them with alcohol as outlined.

Discussion

According to Nishizawa and Winokuti (*2*), sulfonated oil is least soluble as its monosodium compound—i. e., free from soap—and in that form it is entirely insoluble in, or may be completely extracted from, saturated solutions of either sodium chloride or sodium sulfate. Hence in the procedure enough acid is added to the sample before extracting just to decompose the soap. A very slight excess of acid is permissible. Sodium chloride rather than sulfate is used for the first few washes because it gives a much sharper color change with methyl orange and because the salt does not tend to crystallize. The purpose of the final wash with sodium sulfate is to dehydrate the ether extract as much as possible.

The addition of caustic soda to samples of sulfonated oil containing ammonia is required only where the combined SO_3H group is partly or wholly neutralized by the ammonia. In that case unless converted into the sodium salt there would be a loss of combined sulfate due to the volatilization of the ammonium salt upon being ignited. Ammonium soaps, however, do not interfere with the regular procedure.

In the presence of sodium acetate, the acidification as outlined probably decomposes the acetate incompletely into acetic acid, which is partly extracted by the ether. This does not interfere with the method, since during ignition the acetic acid is entirely volatilized. The ether layer probably becomes contaminated also with some of the undecomposed sodium acetate which, however, is removed together with other foreign inorganic salts by the Glauber's salt wash and during the chilling process.

Analysis of Samples

To test the possibilities of the new method in the case of the ordinary commercial sulfonated oils and similar products containing sodium acetate, the committee was requested to analyze two samples of sulfonated oils, samples B and B-1, by both the sulfuric acid titration method and the new ash-gravimetric method. The results are given in Table I. Sample B was a highly concentrated sulfonated (sulfated) castor oil and sample B-1 was a mixture of equal parts of sample B and a 5 per cent solution of anhydrous sodium acetate. In the case of sample B-1 the committee reported unanimously that accurate end points were impossible; hence, no data are listed under the sulfuric acid titration method.

Table I. Determination of Combined Sulfuric Anhydride in Sulfonated Oils by New and Old Methods

Sample B					Sample B-1			
	Ash-gravimetric method			Sulfuric acid titration method		Ash-gravimetric method		
Analyst	I	II	Av.	Av.	Analyst	I	II	Av.
	%	%	%	%		%	%	%
1	5.37	5.37	5.37	5.24	1	2.51	2.58	2.55
2	..	..	..	5.39	3	2.48	2.52	2.50
3	5.05	4.98	5.02	5.18	4	2.52	2.50	2.51
5	..	..	..	5.26	5	2.51	2.57	2.54
6	5.04	5.10	5.07	5.10	6	2.65	2.54	2.60
7	5.26	5.18	5.22	5.16	7	2.63	2.64	2.64
8	5.22	5.17	5.20	5.17	8	2.67	2.61	2.64
9	5.20	5.24	5.22	5.25	9	2.50	2.54	2.52
10	5.27	5.29	5.28	5.19	10	2.46	2.57	2.51
Mean			5.20	5.22				2.56[a]
Greatest difference			0.35	0.29				0.14
Average deviation			0.09	0.06				0.05

[a] By calculation, 2.60.

It will be noticed that the mean for sample B by the new and old methods was 5.20 and 5.22 per cent, respectively; also that for sample B-1 the mean by the new method was 2.56 per cent compared with 2.60 per cent by calculation. It will also be observed that the different analysts obtained good agreement in the results by the new method; thus the greatest differences were 0.35 and 0.14 per cent, and the average deviations were 0.09 and 0.05 per cent, respectively, for samples B and B-1.

Combined Sulfuric Anhydride in Commercial Sulfonated Compounds

Sulfonated products of different types were analyzed in the writer's laboratory by the new method and the results are listed in Table II. Where the method could be used, results by the sulfuric acid titration method are also given. Where it was not possible to compare the two methods, the combined salt water washes by the new method were further extracted with ether or ether-alcohol, but in all cases the residues in the extracts were found to be negligible. Furthermore, the ash invariably gave a negative test for chloride, indicating the probability that the ether extracts were free from Glauber's salt. Because of troublesome emulsions with samples 4, 5, 6, and 7, the combined sulfuric anhydride in these products was determined by procedure C.

Table II. Determination of Organically Combined Sulfuric Anhydride in Sulfonated Compounds

Sample	Description	Ash-Gravimetric Method	Sulfuric Acid Titration Method
		%	%
1	Sulfated castor oil	5.23	5.19
2	Sulfated castor oil[a]	2.58[b]	...
3	Sulfated olive oil[c]	3.90	3.82
4	Sulfonated oil[d]	3.00	0.00
5	Sulfated fatty alcohol	16.18	15.80
6	Sulfonated fatty ester[e]	6.25	0.00
7	Sulfonated aromatic hydrocarbon[f]	10.70	0.00
8	Sulfonated mineral oil	14.21	0.00
9	Sulfonated mineral oil[g]	4.88[h]	0.00

[a] Equal parts of sample 1 and 5 per cent solution of sodium acetate.
[b] By calculation 2.60.
[c] Neutralized with ammonia.
[d] Saponifiable, true sulfonic acid type.
[e] Fatty acid combined with sulfo-alkylamine.
[f] Isobutyl naphthalene sodium sulfonate.
[g] One part of sample 8 and two parts of 25% solution of Na_2SO_4.
[h] By calculation 4.74.

Summary

A new gravimetric method, called the "ash-gravimetric" method, is outlined for the determination of organically combined sulfuric anhydride in sulfonated oils. The method is direct and seems to be applicable to all types of sulfonated oils, including: the sulfate or ester type, with or without titrable salts; sulfonated saponifiable oils (true sulfonic type); sulfonated mineral oils; sulfonated aromatic hydrocarbons; and sulfonated or sulfated fatty alcohols and esters —the last two being soap substitutes recently brought on the market. In many of these cases the present sulfuric acid titration method is not applicable. In the new method only one sample is required for analysis, compared with two by the other methods. The manipulations are comparatively simple, check results are easily obtained, and the concordance among different analysts is very satisfactory.

Acknowledgment

The writer wishes to express his appreciation to M. B. Hart of this laboratory for assistance with the analytical work, and to L. A. Olney, chairman of the Research Committee of the American Association of Textile Chemists and Colorists, under whose guidance the subcommittee on sulfonated oils is working.

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Inhibiting Effect of Certain Substances upon Oxidation of Sulfurous Acid

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THE literature regarding the determination of sulfurous acid contains many indications that incomplete recovery may be due to oxidation of sulfite or bisulfite to sulfate. Many of these have been summarized by Monier-Williams (*3*). Among the substances mentioned early as hastening the oxidation are included oxalic acid, carbon dioxide, ozone, and copper. Among substances reported as retarding the oxidation are mannitol, benzaldehyde, ethyl alcohol, glycerol, benzylic alcohol, sucrose, invert sugar, asparagine, aspartic and glutamic acids, potassium lactate, and stannous and stannic chlorides. Recently Kolthoff (*2*) has published observations on a number of the above substances and also on manganous and ferrous ions, glucose, lactose, and boric acid in the oxidation of 0.05 *M* sodium sulfite and sodium bisulfite solutions standing at room temperature.

Waterman (*5*) observed that excess alkali increased the oxidation of sodium sulfite. Observation that sodium sulfite oxidized more rapidly than sulfurous acid solutions led Nichols and Reed (*4*) to choose the latter as a reference substance in distillation experiments.

Experiments with Sulfurous Acid Solutions

It was thought desirable to extend to sulfurous acid solutions a study of some of the substances used with sulfite and bisulfite solutions by Kolthoff. This study[1] was carried out as follows:

The sulfurous solutions were prepared by passing sulfur dioxide gas from a cylinder into distilled water and diluting to the desired strength. For each substance studied, 50 cc. of the diluted solution were made up in a 500-cc. volumetric flask. After thorough mixing, this was divided equally by means of a 250-cc. volumetric flask and each portion poured gently into a 500-cc. Erlenmeyer flask containing one of the substances in the amount indicated in Table I. Where necessary the flasks were rotated gently to cause the inhibitor to go into solution as far as possible. The flasks were closed with paraffined cork stoppers and kept in a dark cupboard at room temperature between observations.

Table I. Decomposition of 0.0573 *M* Sulfurous Acid at Room Temperature

Substance Added to 250 cc. of Solution	Diminution of Titer of Sulfurous Acid Solution 8 days	16 days	23 days
	%	%	%
5.0 g. sucrose	3	12	16
5.0 g. mannitol	2	12[a]	18[a]
5.0 g. lactose	6	14	18
5.0 cc. glycerol	3	13	18
0.05 g. stannous chloride	12	20	23[a]
0.5 g. stannic chloride	10	20	27[a]
10.0 cc. ethyl alcohol	9[a]	22[b]	32[b]
20.0 mg. Cu ion (cupric tartrate)	15	28	37
0.5 g. $SnCl_4$ and 0.5 g. H_3PO_4	15	27[a]	39
3.0 g. boric acid	16	31	41
0.5 g. molybdic acid	17	33	44
0.5 g. boric acid	22	40[b]	47[b]
No addition	17	42	52[b]
10.0 mg. ferrous ion (sulfate) and 1.0 g. H_3PO_4	40	79	[c]
50.0 mg. ferrous ion (sulfate)	75	[c]	[c]

[a] Duplicate determinations differed from mean by more than 2 per cent.
[b] Duplicate determinations differed from mean by more than 5 per cent.
[c] Remaining solution insufficient for titration.

The initial concentration of sulfurous acid was 0.0573 *N*. The per cent loss in concentration of sulfurous acid as shown by titration into 0.1 *N* iodine after 8, 16, and 23 days is shown in Table I, the substances added being listed in order of their effectiveness in preventing oxidation at the time of the last observations.

Several of the inhibitors that appeared to be effective at room temperature were next used in the distillation of sulfurous acid into iodine, using the method and apparatus described by Nichols and Reed (*4*).

The sulfurous acid solutions were prepared as before by bubbling sulfur dioxide from a cylinder through distilled water and diluting to the desired strength. Of the diluted solutions 10 cc. were introduced into an 800-cc. Kjeldahl flask which was immediately connected, through a condenser and adapter, to a 500-cc. Erlenmeyer flask standing in an ice-water bath and containing 50 cc. of approximately 0.1 *N* iodine solution. Through a vent tube with a narrow tip dipping below the solution in the Kjeldahl flask were then added in succession 10 cc. of 10 per cent sodium bicarbonate and 10 cc. of concentrated hydrochloric acid. Following these additions, 150 cc. were distilled over into the receiving flask, and the residual iodine was titrated with 0.1 *N* sodium thiosulfate. Blank determinations were made in a similar manner in all cases, omitting only the sulfurous acid solution, and the corrections were applied before calculating the per cent recovery.

The results are given in Table II, showing in each case the calculated probable error of the mean percentage recovery.

Table II. Effect of Inhibitors on Percentage of Sulfurous Acid Distilled from Sulfurous Acid Solutions

Inhibitor Added Kind	Amount	Blank Correction as SO_2	SO_2 Recovered
	Grams	*Gram*	%
None	....	−0.0006	92.7 ± 0.8
Dextrose	6	+0.0003	103.8 ± 1.0
Sucrose	6	−0.0006	97.9 ± 0.2
Tartaric acid	6	−0.0004	98.3 ± 1.1
	Cc.		
Glycerol	10	+0.0002	89.5 ± 1.8
Benzyl alcohol	2	−0.0004	94.9 ± 3.9
Ethyl alcohol	10	−0.0099	82.2 ± 3.2
Mannite	6 grams	−0.0001	104.0 ± 2.2

Experiments with Dried Fruit

The inhibitors used with sulfurous acid solutions were employed in the determination of sulfurous acid in several samples of dried fruit, using the method described above. The results corrected for blanks and with the probable errors of the means are shown in Table III, with the exception that mannite was tried with only one sample of fruit (apricots). In this case the corrected value was 490 p. p. m. ± 3 without the inhibitor, and 493 p. p. m. ± 2 with the addition of 6 grams of mannitol.

Jeu and Alyea (*1*) have reported that hydroquinone and other phenols exert a powerful retarding effect upon the oxidation of sulfite under the conditions of their experiments; hence several of these were tried in the distillation of sulfurous acid from dried fruits. Metallic zinc (dust) and tin (mossy) were also tried, as was the addition of a layer of refined mineral oil (Nujol). The equivalent ratio of sulfur dioxide to phenol in the experiments with apricot sample 2 was 25; with pears it was 18; with apricot sample 1 it was 0.9 and 4.5 (pyrogallol). The results are given in Table IV, in which as in preceding tables the probable errors of the means are also shown.

[1] Begun by C. M. Wiedmann in this laboratory.

TABLE III. EFFECT OF INHIBITORS ON AMOUNT OF SULFUROUS ACID DISTILLED FROM FRUIT

Inhibitor Added		Sulfur Dioxide					
		Apples		Apricots		Peaches	
Kind	Amount	Found	Increase	Found	Increase	Found	Increase
	Grams	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
None	..	809 ± 2	...	1877 ± 23	...	1891 ± 12	...
Dextrose	6	839 ± 12	30	1914 ± 0	37	1812 ± 19	− 79
Sucrose	6	830 ± 6	21	.....	...	1867 ± 17	− 24
Tartaric acid	6	801 ± 20	− 8	1902 ± 12	25	1728 ± 32	−163
	Cc.						
Glycerol	10	852 ± 16	43	1899 ± 3	22	1884 ± 6	− 7
Benzyl alcohol	10	683 ± 8	−171	1607 ± 68	−270	.....	...
Ethyl alcohol	10	539 ± 0	−270	1699 ± 2	−178	1549 ± 76	−342

TABLE IV. EFFECT OF INHIBITORS ON AMOUNT OF SULFUROUS ACID DISTILLED FROM FRUIT

Inhibitor Added		Sulfur Dioxide					
		Apricots 1		Apricots 2		Pears	
Kind	Amount	Found	Increase	Found	Increase	Found	Increase
	Gram	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
None	.....	436 ± 20	..	2646 ± 2	...	1786 ± 52	...
Catechol	0.0055	....	..	2559 ± 3	− 87	.....	...
Resorcinol	0.0055	....	..	2537 ± 8	−109	.....	...
Hydroquinone	0.0055	....	..	2602 ± 3	− 44	.....	...
Hydroquinone	0.0275	455 ± 0	19	.....	...	.....	...
Pyrogallol	0.0042	419 ± 3	−17	2654 ± 48	8	1725 ± 0	61
Pyrogallol	0.0210	465 ± 4	29	.....	...	.....	...
Phloroglucinol[a]	0.0054	....	..	2664 ± 15	18	.....	...
Zinc, metallic	0.2	425 ± 11	−11	1845 ± 6	−801	.....	...
Tin, metallic	0.36	440 ± 5	4	.....	...	1822 ± 25	36
	Cc.						
Mineral oil	50	....	..	.....	...	1720 ± 31	− 66
Ethyl alcohol	10	....	..	.....	...	1584 ± 27	−202

[a] Including water of crystallization.

DISCUSSION

In the experiments with the sulfurous acid standing at room temperature the inhibiting or accelerating effects of the different added substances were in a general way similar to those reported by Kolthoff for sodium sulfite and bisulfite. Only ferrous ion had a definite accelerating effect. All the other added substances appeared to have more or less inhibiting effect, although in several cases the differences are probably too small to be of significance. Sucrose, mannitol, lactose, and glycerol had effects of undoubted significance, reducing the oxidation by two-thirds or more. While stannous and stannic chlorides and ethyl alcohol were less effective, even these substances reduced the oxidation by half or more.

In the distillation experiments with sulfurous acid solutions mannitol, dextrose, tartaric acid, and sucrose increased the recovery by an apparently significant amount. Benzyl alcohol was of doubtful effect and the determinations made with this inhibitor were noticeably erratic. Glycerol was also of doubtful value, while ethyl alcohol decreased the yield by a significant amount, although here again the determinations were somewhat erratic. The blank correction for most of the inhibitors used was small, usually amounting to about that for the reagents without inhibitors which is assumed to be due to loss of iodine by volatilization. The small positive corrections for dextrose and glycerol are probably errors. The blank correction for ethyl alcohol, however, is 15 or more times as large as for the other inhibitors, and has the effect of reducing the yield from over 100 to slightly over 80 per cent.

In the distillation of sulfurous acid from dried fruits, the data of Nichols and Reed (*4*) seem to support the conclusion that too high results are unlikely. Hence it is assumed that the highest values obtained by distillation into iodine approach most closely the true values.

Examination of the figures in Tables III and IV indicates that in the distillation of sulfurous acid from dried fruit none of the inhibitors used consistently increased the yield by a significant amount. Benzyl and ethyl alcohols again gave erratic results, and the yields were consistently and significantly lower.

The use of a layer of mineral oil was intended to keep the boiling liquid out of contact with the atmosphere in the distillation flask. This failed of its purpose, for severe bumping occurred and the layer was not entire during boiling; the oil separated in several large globules or agglomerations.

Quite commonly during distillation the side walls of the adapter in the receiving flask became coated with a somewhat waxy, yellowish, granular deposit at the surface of the liquid. When apricot sample 2 was being studied with zinc dust this deposit was unusually prominent. In this case the yield of sulfurous acid was remarkably low. The deposit was soluble in carbon bisulfide and was suspected of being sulfur, but was not identified. The occurrence of a deposit of similar appearance in subsequent blank determinations made it appear doubtful if it were free sulfur. When metallic tin was used the deposit was not unusually large. In this connection it is interesting to note that Zerban and Naquin (*6*) reported deposits of free sulfur in tin condensers during the distillation of sulfurous acid.

SUMMARY

Inhibiting effects of various substances noted by Kolthoff in the oxidation of sodium sulfite and bisulfite solutions at room temperature have been found to occur in sulfurous acid solutions. The authors' experiments indicate that none of the substances suggested as sulfite oxidation inhibitors and tried by them are effective in increasing the yield of sulfurous acid distilled from dried fruits.

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THE DISCOVERY that vitamin D is produced by the action of ultra-violet rays on organic substances started experiments to produce or multiply the vitamin in foods. Two German research workers claim to have discovered that prolonged treatment with ultra-violet rays produces poisonous substances.

Determination of Silicon in Sea Water

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THE presence of compounds containing silicon dissolved in natural waters was apparently first noted by Bergman (*3*) in 1770 and the first quantitative data were reported by Bunsen (*4*) in 1847. Three years later, Forchhammer (*7*) noted the presence of silicates in sea water collected near Copenhagen. In 1891 Murray and Irvine (*11*) summarized the quantitative data of other investigators on the silicon content of sea water, elaborated considerably on previous work, and attempted to show the role of the compounds containing silicon in the sea. This pioneer work may now be criticized because of the admitted lack of suitable analytical refinement and the failure to prevent contamination of the water samples. In 1905 Raben (*12*) made a detailed study of the determination of silicon in sea water using a gravimetric method which has since been improved by Wells (*18*). This procedure is undoubtedly the most reliable of the gravimetric methods, but the main objections to it are the large supply of water necessary for a determination, the length of time required, and the ease with which a sample may be contaminated.

The first application of a colorimetric method for silicates was that by Jolles and Neurath (*8*). These investigators used as their reagents concentrated nitric acid and a 16 per cent solution of potassium molybdate. The yellow color, developed by the formation of the silicomolybdate complex, was shown to reach maximum intensity when heated for a short interval. Solutions of water glass of known silicon content, accorded the same treatment as the samples, were used as standards. Later workers (*10, 13, 14*) eliminated heating and substituted the use of other mineral acids. In 1914 Winkler (*19*) introduced the use of potassium chromate solutions as artificial color standards and thus avoided any contamination of water-glass standards by glass vessels. Dienert and Wandenbulke (*6*) modified Winkler's procedure by the introduction of standards prepared from picric acid solutions. Atkins (*2*) showed that the colorimetric method was applicable to sea water, while the preparation of the picric acid standards for such determinations has been made the subject of investigation by King and Lucas (*9*).

COLORIMETRIC DETERMINATION OF SILICON

The chemistry of the method, as shown by Asch (*1*), depends upon the formation of a yellow heteropoly acid, having the probable formula of $H_8Si(Mo_2O_7)_6$ when an acidified solution of a soluble silicate is treated with ammonium molybdate. The method is accurate and is particularly advantageous because of the small amount of sample required and the ease and rapidity of manipulation. The procedure and preparation of the reagents required are as follows:

AMMONIUM MOLYBDATE REAGENT. Ten grams of ammonium molybdate are dissolved in 90 grams of distilled water. The heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, is the usual compound employed for this reagent and should be examined from time to time to insure freedom from silicates.

PREPARATION OF PURE PICRIC ACID. Forty grams of picric acid are dissolved in 100 ml. of benzene on a water bath. The resulting solution is filtered with suction through a Büchner funnel, leaving behind by decantation as much water as possible. The benzene is then partially evaporated, under reduced pressure, until water again appears in dark globules. These globules are decanted off and the excess benzene evaporated completely at reduced pressure, until the picric acid is dry and free from benzene. The drying under reduced pressure is performed on a water bath. Small quantities of picric acid are placed in clean, dry test tubes, and the tubes are sealed and stored until ready for use.

PREPARATION OF PICRIC ACID STANDARDS. A solution is prepared by dissolving 314.2 mg. of the vacuum-dried, recrystallized picric acid in distilled water and making up to a volume of exactly 1 liter. This solution has a color equivalent of 10 mg.-atoms of silicon per kilogram for sea water of chlorinities from 14.5 to 19.5 per mille. Fifty milliliters of the solution are diluted to a volume of 1 liter and portions of it are taken and diluted in volumetric flasks to 250 ml. Four milliliters of the picric acid solution, when diluted to 250 ml., are equivalent to 0.008 mg.-atoms of silicon per kg. when a 50-ml. Nessler tube is filled to the graduation. Solutions with different portions of picric acid are thus prepared and transferred to glass-stoppered bottles. When standards are desired, a series of 50-ml. Nessler tubes are filled to the mark with these solutions. Each increase of 2 ml. of the picric acid on dilution to 250 ml. gives an increase of 0.004 mg.-atoms of silicon per kg. A series of such standards is most convenient for field work and is stable over a considerable period of time.

If it is desired to report as milligram-atoms of silicon per liter, the original picric acid solution should contain 307.5 mg. of picric acid per liter instead of 314.2 mg.

METHOD. To 50 ml. of freshly sampled sea water, secured directly from the sampling apparatus as it arrives aboard ship, 2 ml. of the ammonium molybdate reagent are added and 4 drops of 18 *N* sulfuric acid. After 5 minutes, the resulting color is compared either with a picric acid standard in a colorimeter or with a series of standard solutions in Nessler tubes.

FURTHER EXPERIMENTAL INVESTIGATIONS

A study of four possible factors that might influence the colorimetric determination of silicon in sea water was made and the observations noted are summarized below.

POSSIBLE DIFFERENCES IN BEHAVIOR OF META- AND ORTHOSILICATES. To ascertain whether an inherent error in the determination may be encountered when different ions containing silicon are present, two standard solutions, one of sodium metasilicate and the other of sodium orthosilicate, were prepared. Weighed amounts of pure silica were fused with sodium carbonate and sodium hydroxide, respectively. The fused masses were dissolved in water, neutralized, and each diluted to a volume of 1 liter. Immediate analysis of these solutions colorimetrically gave the following:

	Silica	
	True value	Value obtained
	Mg.-at./l.	*Mg.-at./l.*
Orthosilicate	0.083	0.082
Metasilicate	0.083	0.082

These data were explained by the fact that one atom of silicon occurs in the ortho ion as well as in the meta ion and thus the same coördination of the silicon atoms with the molybdate radicals takes place and develops the same color intensity.

EFFECT OF TEMPERATURE ON SILICOMOLYBDATE COLOR. A series of samples containing the same amount of silicon was run at various temperatures from 7° to 25° C., but change in color intensity could not be detected with either the samples or the standard picric acid solutions.

EFFECT OF FUNGUS GROWTHS IN PICRIC ACID STANDARDS. A fungus growth was noticed in several picric acid standard solutions and the colonies started were permitted to continue. Three months later, on dilution of the standard and comparison with freshly prepared solutions, no diminution in color intensity was discernible.

EFFECT OF LONG STANDING ON PICRIC ACID STANDARDS. Picric acid solutions to be used for the preparation of standards were made in March, 1930. They were allowed to stand 17 months, part of the time subjected to the action of sunlight. In August, 1931, these samples were diluted in the

usual manner and compared with freshly prepared solutions. No change whatsoever was observable. One year later (August, 1932), standards were again made from these solutions and compared with those freshly prepared and no change was noted. This fact appears to contradict the observations reported by Atkins (*2*), who noted a change in 3 months, but the authors have likewise observed that continual exposure of the diluted solution to the dust of the air, etc., may cause a fading in color within the period mentioned by Atkins. However, these diluted solutions may be kept for a considerable period in stoppered tubes, the stoppers being removed only when comparisons are to be made.

Use of Colorimetric Method

As the result of a detailed study of the method used in the laboratory and aboard ship, the following notes summarize certain observations and precautions necessary in the application of the method:

1. A greenish tinge is sometimes obtained with water having more than 0.07 mg.-atoms of silicon per kg., especially if Nessler tubes are employed. This interference may usually be eliminated by the use of the colorimeter or by the reduction of the size of the sample to 25 ml.
2. With waters of low silicon values, 100-ml. samples should be utilized. A sensitivity is obtained with Nessler tube series of 2 parts of silicon to 100,000,000 parts of water.
3. An excess of sulfuric acid causes a diminution in the color intensity, but no effect is noted with slight excesses of the molybdate solution. The yellow color of the heteropoly acid reaches its maximum intensity within 5 minutes after the addition of the reagents and remains constant for nearly 3 hours. However, the samples should be compared with the standards as soon as possible to avoid any increase in silicates caused by the dissolving action of the sea water on the glass container.
4. A maximum probable error of 5 per cent occurs when Nessler tubes are employed and this may be reduced by the employment of the colorimeter.
5. Dissolved compounds containing iron or phosphorus in sufficient quantities to affect the determination are not encountered in sea water (*1*, *15*).
6. Organisms and finely divided inorganic material, if present in sufficient quantities, may be removed by filtration or centrifuging.
7. Contamination from glass bottles containing the sea water samples is very marked, as shown by Atkins (*2*) and Thompson and Johnson (*17*). Thus water that has been exposed to glass for some length of time should not be analyzed for silicon. If containers other than glass are employed, they soon corrode and the sediment settling to the bottom may absorb silicates. Thus for reliable results analyses should be performed only on freshly sampled sea water.
8. The C. P. picric acid contains varying quantities of water, and such material should never be used for the preparation of standards without recrystallization and drying.
9. Picric acid standards should never be prepared with sea water, as the dissolved salts have a very pronounced "salt effect."
10. Should it be deemed advisable to dilute samples with distilled water, an examination of the latter for silicon should first be made.
11. To insure concordant results on long trips, it is advantageous to prepare two standard stock solutions from two different batches of pure picric acid. The comparison standards are made from one of these solutions and these are checked occasionally against the second standard.
12. Various means of reporting the quantity of dissolved silicates in sea water occur in the literature. The authors feel that the most logical form of reporting the results is that recommended by a committee of chemists representing the different marine and oceanographic institutions on the Pacific Coast of Canada and the United States. The committee recommended that the constituents of sea water be reported as milligram-atoms of the element determined per kilogram of water. A milligram-atom is defined as the result obtained when the number of milligrams of the determined element per kilogram of sea water is divided by the atomic weight of the element (*5*).
13. The silicon content varies considerably in sea water ranging from less than 0.01 mg.-atom of silicon per kg. in surface waters where there is marked plankton growth to as high as 0.3 mg.-atom in the bottom ocean waters. Generally speaking, the silicon content increases with depth, and coastal waters as well as those of estuaries will show a seasonal fluctuation.

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Note on Shaffer and Hartmann Combined Carbonate-Citrate Method for Determination of Glucose

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In many respects one of the most rapid and convenient methods for the determination of dextrose after the hydrolysis of starch by a malt solution is that of Shaffer and Hartmann[1] in which the "combined carbonate-citrate solution" is used. This is a single stable alkaline copper solution to which is added sufficient potassium iodide and potassium iodate to yield a 0.1 *N* iodine solution when acidified. With this combined reagent it is necessary only to add the dextrose solution, boil, cool, acidify, and titrate the excess iodine liberated.

In checking this method with a washed starch and also against dextrose (No. 41, Bureau of Standards), the amount recovered for the latter, calculated from the copper : glucose ratios of Shaffer and Hartmann, averaged 2.3 mg. more than that started with. In other words, in the authors' hands and under their conditions, with the standardization of uniform heating by an electric hot plate[2] in bringing the solution to a boil, there was somewhat more reduction from a given amount of glucose than that reported by Shaffer and Hartmann.

A preliminary examination of the data showed that there

[1] Shaffer, P. A., and Hartmann, A. F., *J. Biol. Chem.*, **45**, 365 (1921).

[2] I. D. Jones has found that the rate of heating by the slightly fluctuating electric current may be readily controlled by the use of an ammeter and rheostat.

was a linear relation between the amounts of dextrose present and the amount of copper reduced. In order to derive an expression of this relation which would be more applicable under the authors' conditions than the published ratios, a straight line was fitted by the method of least squares to the results of 46 determinations (omitted).

This linear estimating equation was found to be:

Mg. of glucose = 0.458 (mg. of copper reduced) − 1.546, with a standard error of 0.74 mg. of glucose, over the range between 35 and 125 mg. of glucose.

These data indicate that the combined carbonate-citrate method gives results closely paralleling those published by the authors, but because of the number of factors which affect the reduction each analyst should carefully standardize his technic and for the more accurate work should derive an expression of the relation between the amount of dextrose present and the amount of copper reduced (or set of copper: glucose ratios) which is applicable under the conditions prevailing in his laboratory.

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Continuous Liquid Extractor

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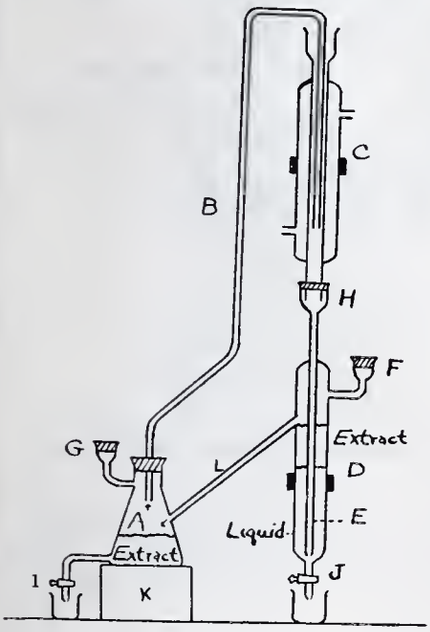
A CONTINUOUS liquid extractor for solvents having a lower specific gravity than the liquid to be extracted is shown in the figure.

The receiving flask *A*, containing the solvent, can be made from a 250-cc. Erlenmeyer flask. The container *D* consists of a large test tube constricted at both ends, the size of the tube varying with the quantity of liquid to be extracted. The side tubes *G* and *F* for filling the receiver and container, as well as *H*, are made by constricting the mouth of a 15 × 1.8 cm. test tube. The glass stopcocks *I* and *J* are used to drain the apparatus. If a glass-blower is available, *H* may be made with a mercury seal connecting the condenser and the container, thus doing away with a stopper. The tube *E* is joined to *D* at the upper end by an inner seal and extends down almost to the bottom of the tube; or, to do away with this inner seal, *E* can be joined to *D* by a stopper at the upper end. The circuit is completed by the tube *L* which joins the receiver *A* and the container *D*.



The solvent (ether) is placed in *A* by means of the side tube *G*. The ether is boiled on the steam bath *K*, vaporizes up *B*, condenses in *C*, and flows down *E*, bubbling up to extract the liquid (some aqueous solution). The ether extract forms a layer on top of the liquid and when it reaches tube *L* flows back into the receiver. Pure ether boils again to extract continuously. After complete extraction, the ether extract may be drained by means of *I* and the liquid removed from *D* by means of *J*.

The apparatus is absolutely stationary and never has to be moved or adjusted. It may be taken apart but can be filled and drained without disassembling very easily. A series of three or four of these extractors may be set up on a steam bath in a small hood. Both receiver and container may be varied in size, depending upon the quantities to be used. The container *D*, however, should be kept narrow, so as to have as much surface of the liquid as possible exposed to the ether bubbles. Complete extraction of a compound difficultly soluble in ether is accomplished in 8 to 10 hours.

Received July 31, 1933.

Apparatus for Filling Large Closed-End Manometers

Angus E. Cameron

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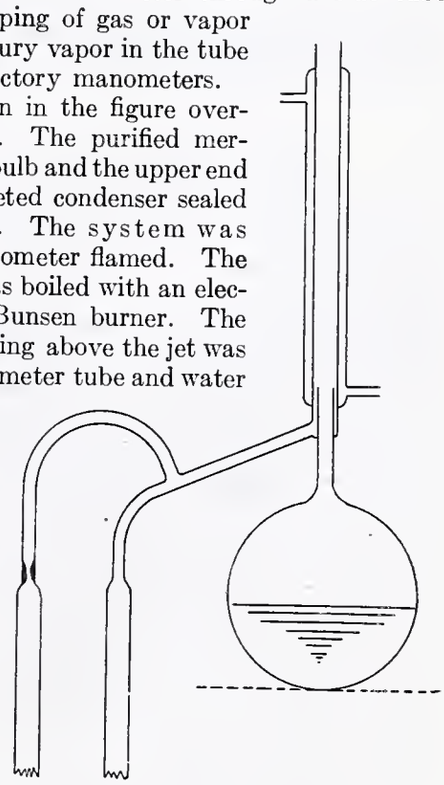
THE ordinary method of filling a closed-end manometer and boiling out gases from the mercury during evacuation is attended with considerable danger of breakage when the manometer is of large bore and sufficient length to enable one to read pressures over a range of one atmosphere. Distillation of mercury into the manometer through a side tube seemed to permit trapping of gas or vapor below the wall of mercury vapor in the tube and result in unsatisfactory manometers.

The apparatus shown in the figure overcomes both difficulties. The purified mercury was placed in the bulb and the upper end of the short water-jacketed condenser sealed to a high-vacuum line. The system was evacuated and the manometer flamed. The mercury in the bulb was boiled with an electric heater or with a Bunsen burner. The mercury vapor condensing above the jet was delivered into the manometer tube and water vapor and gas passed up through the condenser. Once set in operation the system required no attention until sufficient mercury had accumulated in the manometer and then the closed end was sealed off at the strictured portion. Evacuation with a good oil pump should be sufficient to give a well evacuated manometer, since the device used to introduce the mercury is essentially a diffusion pump.

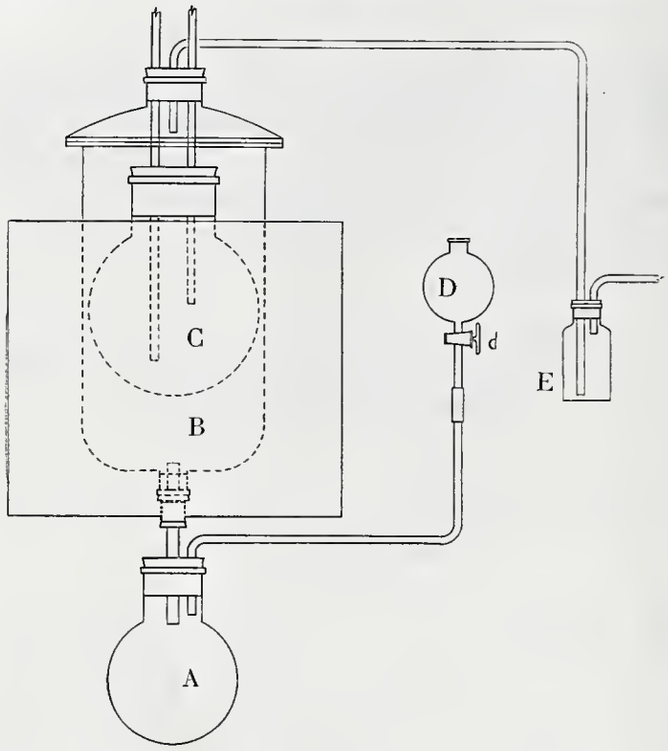


Received August 25, 1933.

Recovery of Iodine from Metallic Iodides by Oxidation with Technical Nitric Acid

Rush Fox McCleary and Ed. F. Degering, Chemical Laboratory, Purdue University, Lafayette, Ind.

In the preparation of zinc ethyl in this laboratory, it seemed advisable to devise a simple procedure for the recovery of iodine from the zinc iodide residues. The various methods for iodine recovery suggested by Torossian (*6*),



Stephenson (*5*), Arndt (*1*), Kleinstück and Koch (*2*), and Puig (*4*) are applicable to solutions or finely divided solids, and are not readily adapted to the recovery of iodine from a zinc iodide cake. The procedure proposed by Lachman (*3*) involves the hazard of breaking the flask while crushing the hard cake of zinc iodide and unreacted zinc, and the procedure is a little involved. The apparatus shown in the figure eliminates this hazard, and also has the advantage of a simple procedure which gives a good initial yield of crude iodine.

Flask *A* contains the hard residue from the zinc ethyl distillation. *B* is an ordinary bell jar fitted with a ground-glass lid, and is surrounded by an ice bath. The system may be kept slightly evacuated through the water trap *E* by partially closing stopcock *d*. Crude concentrated nitric acid in slight excess of the calculated amount is introduced into flask *A*, in small portions, through funnel *D*. Stopcock *d* is left partly open and air is slowly and continuously drawn through the water trap *E*. This entrains the iodine vapors efficiently into the bell jar. Iodine which collects on the walls of flask *A* is easily removed by heating gently with a direct flame. Flask *C* is kept cool by means of circulating tap water.

In a recovery of zinc iodide residues which were calculated to contain 315.8 grams of iodine, 308.7 grams of crude iodine were recovered in the initial sublimation. This initial sublimate showed a purity of 90.83 per cent when titrated with standardized thiosulfate solution. By resublimation in the same apparatus, additional purification may be effected.

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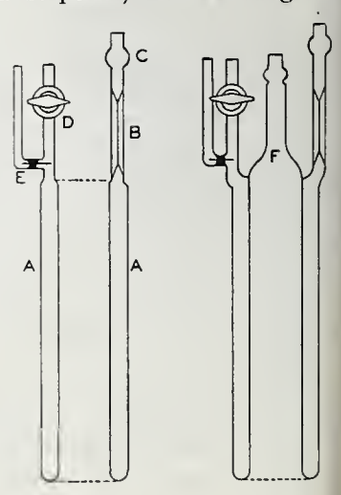
Modified Design for Mercury Bulb of Thermostat

G. B. Heisig and A. E. Cameron, School of Chemistry, University of Minnesota, Minneapolis, Minn.

The conventional thermostat regulator bulb is filled with toluene, and expansion of the toluene causes a change in height of a mercury column which makes or breaks the relay circuit. In spite of the smaller thermal expansion of mercury it is preferable as liquid for a control bulb because creeping of the setting due to seepage of toluene past the mercury column is avoided. Since only the layer of mercury which is in contact with the glass of the bulb can be effective for small and comparatively rapid fluctuations in bath temperature, it is desirable that the surface of the bulb be large. Filling a large bulb with mercury entails a considerable expense and supporting the heavy and rather fragile bulb becomes inconvenient. The authors have designed and used a bulb which is mercury-filled, has a large surface, and yet uses a small amount of mercury.

Two pieces of Pyrex tubing, as thin-walled as was consistent with mechanical strength, of diameters 3.5 and 2.5 cm., respectively, were placed one inside the other and sealed together at the ends to form a double-walled cylinder, a longitudinal section of which is shown at *A* in the accompanying sketch. A capillary tube, *B*, of 0.8-mm. bore was sealed to one end of the cylinder. A small bulb, *C*, was provided to catch any overflow of mercury from the capillary. For the adjustable contact an iron or platinum wire was inserted into this capillary. Diametrically opposite the capillary was sealed a stopcock, *D*. A tungsten wire was sealed through the stopcock arm from a side tube, *E*. The side tube was filled with mercury and a wire dipped into it to make contact to the mercury in the control bulb. The bulb was filled by evacuating it and running clean, dry mercury in through the capillary or through the stopcock, as was most convenient. The quantity of mercury in the bulb could be varied by opening the stopcock and allowing mercury to run into the bulb from the tube above the stopcock or by sucking mercury out of the bulb into this reservoir.



The control was immersed in the thermostat up to the stopcock key in such a location that water from the stirrer was circulated through the inside and around the outside of the cylinder. Using this control bulb and a radio tube relay device, the temperature of a 25-liter thermostat was maintained at 25° ± 0.002° C. A modification of the original design was suggested to one of the authors by Doctor Kingslake of the Institute of Applied Optics at the University of Rochester (New York). The inner tube of the cylinder was extended and drawn down as indicated at *F* to permit a hose to be attached to it. Water could then be drawn through the center of the bulb for use in maintaining a constant temperature in an apparatus which could not be immersed in a thermostat.

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Improved Lamp for Determination of Sulfur in Light Petroleum Products

E. R. Gillis, Casper Laboratory, Standard Oil Co., Casper, Wyo.

It is generally realized that the flame of the standard A. S. T. M. lamp is not readily controlled. This causes considerable loss of time, annoyance, and some inaccuracy in determining sulfurs by method D90-30T. Substitute lamps such as the Vapor Cresolene lamp (made by the Vapo-Cresolene Co., 62 Cortlandt St., New York, N. Y.) allow of ready flame control but have serious faults; the metal burner becomes very hot and causes undue evaporation of volatile oils such as light gasoline. This causes falsely low sulfur determinations and also makes it almost impossible to check results on such light petroleum products.

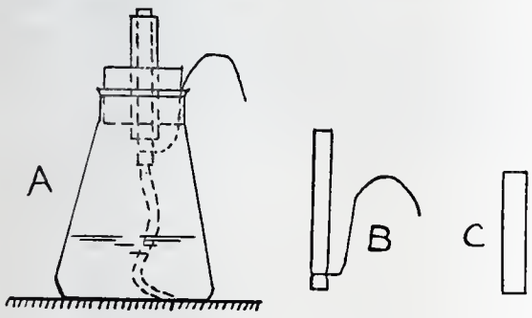

Figure 1. Improved Lamp

A, lamp completely assembled
B, adjusted sleeve with wire control. Approximate tubing size 0.125 × 2 inches (0.3 × 5 cm.)
C, outer tubing, approximately 1.5 inches (3.75 cm.) long and sufficiently large to slip over adjusting sleeve

The Edgar and Calingaert (*1*) lamp is very satisfactory but is not readily available in all laboratories and is not, properly speaking, an A. S. T. M. lamp. A slight modification of the regular A. S. T. M. lamp has been devised in this laboratory which is easily made by anyone and allows ready regulation of flame size without the necessity of taking the lamp from under the chimney.

The single piece of glass tubing of the regular A. S. T. M. lamp has been replaced by two pieces of different size, one within the other. The smaller piece is the same inside diameter as the old single piece and is recessed slightly near the bottom to allow a piece of fine wire about 7.5 cm. (3 inches) long and 0.5 mm. (0.020 inch) in diameter to be twisted around it. The larger piece is of sufficient size just to allow the smaller to slip freely within the larger. The larger, or outside piece of glass tubing, is held tightly in the cork. The smaller piece extends through and projects out of the larger at the bottom about 1.25 cm. (0.5 inch). To regulate the flame, the smaller piece which holds the wick is raised or lowered inside the larger by the wire which extends up through a groove in the cork. This groove is small enough to hold the wire by friction, which in turn holds the glass sleeve at any set position. Any vapors from light gasoline that pass up between the inner and outer tubing are burned in the flame along with gasoline fed through the wick. In other words, the vent for this lamp is the small annular space between the two pieces of glass tubing. The flame of course remains at the top of the larger piece at all times.

The author has run several samples of winter-grade gasoline and others even more volatile, using this new lamp, and finds that it gives very good results and requires much less attention than does the regular A. S. T. M. lamp. Some comparative results on the improved type of lamp and on the standard A. S. T. M. lamp are given below. Four runs were made with each type of lamp, using a cracked winter-grade gasoline of high sulfur content.

Improved Lamp Sulfur	A. S. T. M. Lamp Sulfur
%	%
0.249	0.240
0.255	0.209
0.252	0.237
0.247	Too badly smoked to titrate

None of the lamps of the improved type needed any adjusting or attention after the first 10 minutes of burning, while the A. S. T. M. lamps required full attention from the start until the finish of the burn. In the author's opinion, this new lamp is in many ways superior to the A. S. T. M. lamp for running gasolines of high volatility, and works equally well on heavy gasolines and illuminating oils.

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Received August 5, 1933.

Stirring Rod with Fritted Glass Disk

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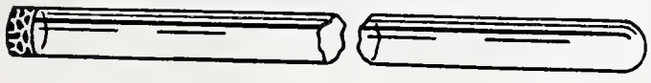
For general use, the author has designed a stirring rod with a disk of fritted glass fused onto an end. The rod was made by the Jena Glass Works of Schott und Gen. and



found to be highly serviceable in boiling off the excessive bromine during Eschka's sulfur determination and in similar operations. The rod is, however, not recommended for quantitative work where precipitation is involved, as precipitate is liable to lodge in the fritted glass.

Received September 26, 1933.

Qualitative Analysis of the Hydrogen Sulfide Group without Ammonium Polysulfide

Ralph W. Hufferd, DePauw University, Greencastle, Ind.

THE common practice in qualitative analysis is to oxidize the elements of the tin division of the hydrogen sulfide group to their higher valence with ammonium polysulfide. Because of the instability and variation in concentration of the polysulfide solution, it is not uncommon for stannous sulfide to resist the treatment and remain with the copper division precipitate. There is the added difficulty of having large quantities of the copper division sulfides, especially copper sulfide, carried over into the tin division. Polysulfide also introduces the nuisance of having a large bulk of sulfur mixed with the reprecipitated sulfides of the tin division, often leaving the analyst in doubt as to whether or not there is any sulfide there.

These difficulties can be either avoided or reduced so considerably as to cause no trouble to inexperienced students by the simple expedient of oxidizing the elements with bromine before precipitating them as the sulfides, and then making the division separation with ammonium sulfide. The sulfide is prepared as needed by passing hydrogen sulfide into 6 N ammonium hydroxide. As a precaution against oxidation of hydrogen sulfide to sulfur during precipitation of the sulfides, nitrate ion is destroyed by repeated boiling with 12 N hydrochloric acid.

Evaporate the filtrate from Group I to about 5 cc. but not to dryness. Add 10 cc. of 12 N hydrochloric acid and again evaporate to small volume. Repeat addition of hydrochloric acid and evaporation once or twice. This procedure does not take much time, but by destroying nitrate ion prevents excessive oxidation of hydrogen sulfide during precipitation.

Add 5 cc. of water and, if necessary, heat to dissolve any solid. It is sometimes necessary to add 2 cc. of 6 N hydrochloric acid. Add an excess of saturated bromine water, and boil off excess bromine. About 2 minutes' boiling will usually suffice. Starch-iodide paper can be used if there is any question. In the writer's laboratory the entire preparation is carried out in the 250-cc. Erlenmeyer in which precipitation is to take place. Neutralize the solution with ammonia and 6 N hydrochloric acid. Adjust acidity and volume in the customary manner, and precipitate with hydrogen sulfide.

Transfer the well-washed precipitate on the filter to a small beaker and add 10 cc. of fresh ammonium sulfide solution, prepared by saturating 10 cc. of 6 N ammonium hydroxide with hydrogen sulfide. Heat the beaker in boiling water for 3 minutes, stirring the contents occasionally. Unless the filter paper seems clean, no attempt should be made to remove it, as it will not interfere with the analysis of the copper division precipitate. This treatment will remove 100 mg. each of the three members of the tin division as sulfides.

After filtering and washing, the precipitate is ready for analysis for copper division elements. Precipitate the tin division sulfides from the filtrate in the customary way.

The writer has found that the average student of elementary qualitative analysis can be expected to find 10 mg. of any member of the group in the presence of 100 mg. each of several or all other members of the group.

Received January 18, 1933.

Filtering Device

E. B. Kester, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

CONSIDERABLE time is lost in the laboratory purifying by recrystallization of small quantities of substances, particularly derivatives of organic compounds such as oximes, hydrazones, semi-carbazones, anilides, and the like. Not only must a Büchner or Hirsch funnel and suction flask be arranged and filter paper installed, but precipitates must be transferred back and forth from funnel to flask. Losses are incurred inevitably. Moreover, it frequently happens that a chemist is isolating a product which during the earlier stages of purification melts below room temperature, in which case he finds it difficult if not impossible (without recourse to more elaborate preparations) to carry out a filtration before his product fuses.

The filtering device illustrated eliminates the need of transfers of solids or solid-liquid mixtures. Numerous successive recrystallizations can be carried out in a surprisingly short time with little loss of product save that which brings the mother liquors up to saturation. Filtrations of crystals obtained by chilling in refrigerating media can be conducted in the media. Increased pressure is obtainable over that secured in suction filtrations.

A large Pyrex test tube, preferably of 75 to 80 cc. capacity, is selected, care being taken to obtain one in which the bore is fairly uniform. A plunger of Bakelite, hard rubber, or other inert substance is turned out on a lathe to such dimensions that the plunger has only sufficient clearance to enable it to slip easily up and down the tube. A number of longitudinal pinholes (about 0.7 mm. in diameter) are bored for escape of the liquid.

When a crystallization has been completed, the filtration is accomplished by merely forcing the plunger to the bottom of the tube. This operation should be started slowly to permit a cake to build up that will prevent escape of crystals up the sides and through the orifices, but may be accelerated when such cake has formed. At the end, the plunger may be pressed down with considerable force so that the product is free of excess liquid when the mother liquors are poured off and the plunger has been withdrawn. It can then be washed, triturated, or recrystallized and filtered again in the same container and in the same way as before. Drying is effected by evacuation of the tube or passing a current of air over the cake.

A soft rubber plunger similarly molded affixed to a glass rod is even more satisfactory from the standpoint of cleanness of filtration, but it can only be used in connection with mild solvents. Benzenoid hydrocarbons, for example, rot soft rubber so rapidly there is serious danger of contamination of product, to say nothing of ruination of the device itself.

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